

1130

UC-90d  
LBL-10278  
Preprint  
c.2  
npl.



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

To be published in *Catalysis Science and Technology*

FEB 21 1980

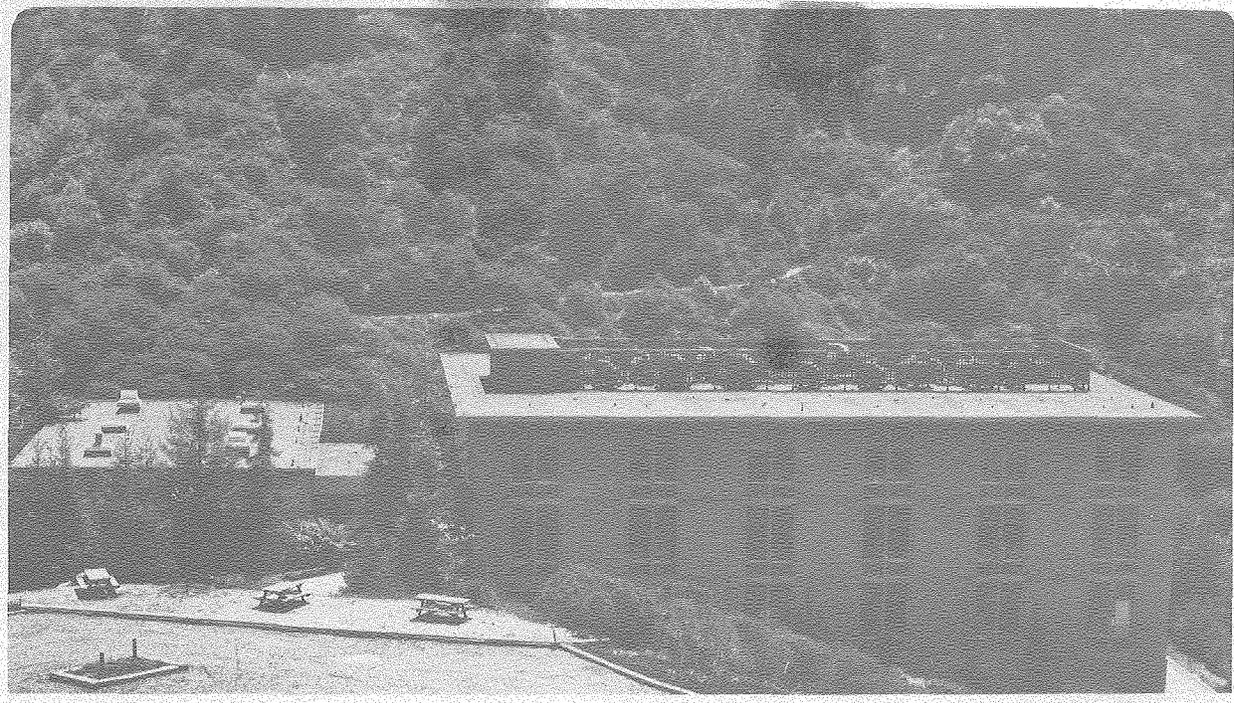
LIBRARY AND  
DOCUMENTS SECTION

A BRIEF HISTORY OF INDUSTRIAL CATALYSIS

Heinz Heinemann

June 1979

**TWO-WEEK LOAN COPY**  
*This is a Library Circulating Copy  
which may be borrowed for two weeks.*



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

LBL-10278 c.2 npl.

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

A BRIEF HISTORY OF  
INDUSTRIAL CATALYSIS

Heinz Heinemann

Lawrence Berkeley Laboratory  
Materials and Molecular Research Division  
University of California  
Berkeley, California 94720

June, 1979



## INDEX A

I	Introduction	1.
II	Catalytic Cracking and Other Acid Catalysed Reactions	4.
III	Zeolite Catalysis	17.
IV	Dual Functional Catalysis	27.
	a) Naphtha Reforming	
	b) Isomerization	
	c) Hydrocracking	
V	Hydrogenation Catalysis and Hydrogen Production	36.
	a) Desulfurization and Denitrification	
	b) Selective Hydrogenation	
	c) Hydrogen Production	
	d) Ammonia Synthesis	
	e) Methanol Synthesis	
VI	Catalytic Hydrocarbon Dehydrogenation	43.
VII	Catalytic Alkylation and Dealkylation	44.
VIII	Catalytic Coal Liquefaction and Gasification	45.
	a) Liquefaction	
	b) Gasification	
	c) Methanation	
IX	Heterogeneous Oxidation, Ammoxidation, Chlorination, and Oxychlorination Catalysis	48.
	a) Oxidation	
	b) Ammoxidation	
	c) Hydrohalogenation and Oxychlorination	
	d) Hydrogencyanide	

X	Olefin Disproportionation Catalysis	52.
XI	Industrial Homogeneous Catalysis	52.
XII	Catalytic Polymerization	57.
XIII	Catalysis for Motor Vehicle Emission Control	60.
XIV	Fuel Cell Catalysis	64.
XV	The Profession of Catalytic Chemist or Engineer	64.
XVI	References	70.

## I INTRODUCTION

Industrial catalysis is an old art. Wine and soap makers have employed catalytic agents for thousands of years, though without knowledge or understanding of their workings. Large-scale conscious use of industrial catalysts originated in the mid-18th century with the introduction of the lead chamber process for manufacture of sulfuric acid, in which nitric acid was used to oxidize  $\text{SO}_2$  to  $\text{SO}_3$  in the presence of water. The lower oxides of nitrogen formed are in turn oxidized with air to form nitric acid. While the need for a catalyst was recognized, the scientific basis for its chemical and kinetic action came only much later. This is a trend that persists to the present. In spite of great advances in the science of catalysis, major industrial applications and novel uses have almost always been based on empirical findings. Scientific explanations followed later and frequently led to process improvements and refinements. The goal of catalytic scientists to be able to predict industrial catalytic behavior of substances and processes has thus far remained elusive. There is hope, however, that with the rapidly increasing sophistication of tools and observational means catalytic science may in the future replace catalytic art.

Mills and Cusumano<sup>( 1 )</sup> have pointed out that the use of catalytic processes has grown almost exponentially from the early 18th century to the present. It has been estimated that at present over 20 percent of all industrial products have underlying catalytic steps in their manufacture. Early catalytic processes were used mostly for the production of inorganic chemicals (sulfuric acid, nitric acid, chlorine, ammonia), with catalytic processes involving organic reactions becoming prominent only in the 20th century, but rapidly dominating the industry, mostly because of the widespread application of catalysis in fuels production.

The present chapter is mostly limited to the rapid growth of industrial catalysis between the second World War and 1978. A few brief excursions into earlier history have been found necessary. The author found it difficult to ascertain exact dates for many innovations. References can in most instances be found for the time of a first commercial operation of a process, but it is much harder and in some cases impossible to determine the time of conception. In fact, the research and development leading to new technology often involves so many people and ideas that the resulting process cannot always be attributed to specific individuals. In addition, publications and even patent application dates frequently lag considerably behind conception.

The great majority of catalytic processes are still based on heterogeneous catalysis. Homogeneously catalysed processes however, have assumed much more importance in recent years and their impact is often underestimated because much of the volume and value of catalytic processes is concentrated in the petroleum refining industry which uses predominantly heterogeneous catalysts. The relative growth of homogeneous catalytic process technology is far greater in chemical and petrochemical applications than in all other industrial applications, including those of the petroleum industry.

While there has been a large number of process developments during the period under consideration, the majority are of an evolutionary type and there are relatively few process ideas that have opened up new chemistry and engineering and/or started new catalytic industries. The list presented in Table 1 gives the author's admittedly subjective impression of what might be called "breakthroughs" in catalytic technology during the last 35-40 years.

Table 1  
Major Catalytic Innovations, 1935-1978

Year of first commercialization	Event	Area of industry
1936	Catalytic cracking	Petroleum
1941	Fluid-bed technology	Petroleum-petrochemicals
1942	Thermoform catalytic cracking	Petroleum
1942	Paraffin alkylation	Petroleum
1950	Catalytic naphtha reforming (Pt-catalysts)	Petroleum
1955	Ziegler-Natta polymerization	Polymers
1960	Acetaldehyde from ethylene (Wacker Chemistry)	Chemicals
1963	Low-pressure ammonia synthesis	Fertilizer
1963	Ammoxidation	Chemicals
1964	Zeolite catalysts	Petroleum-petrochemicals
1964	Oxychlorination	Monomers
1966	Olefin disproportionation	Petrochemicals
1967	Bimetallic reforming catalysts	Petroleum
1968	Shape selective catalysis	Petroleum-petrochemicals
1976	Emission control catalysts	Automotive

All of these will be discussed in this chapter along with many other developments of importance. No claim can be made for completeness.

During the early years of industrial catalysis development described in this chapter, there were several new technologies requiring extensive engineering as well as catalyst developments. Fluid catalytic cracking, catalytic reforming, and low-pressure ammonia synthesis are examples. In the last 15 to 20 years there has been more emphasis on novel catalysts that produced better products and product yields, and which could be used in existing or slightly modified equipment. Examples of this type are zeolite and bimetallic reforming catalysts. A major reason for this trend lies in the spiraling construction costs of industrial plants, with the concomitant increase in the financial risk of failure or protracted break-in periods of novel facilities. A catalyst failure at worst may require a change back to a previously used catalyst, with a loss of some days in down-time, while major equipment changes may require weeks and months during which costly facilities are nonproductive. In addition, there has been a trend to ever larger unit operations. New engineering technology is best tried in relatively small units, which however, are no longer competitive with large production facilities. One can expect the trend to improve older catalysts, and introduce novel catalysts, in existing equipment to continue for some time.

To support the importance of heterogeneous catalysis to industrial production, three tables illustrate catalytic uses: for the Petroleum Industry in the U.S.A. (Table A), giving capacities, catalyst sales and values; for the Petrochemical Industry (Table B)<sup>x</sup> giving product volume and value; and for the Commodity Chemicals Industry (Table C)<sup>x</sup> giving product volume and value. A similar table on industrial homogeneous catalytic uses is contained in the chapter XI (Homogeneous Catalysis, Table 5).

## II CATALYTIC CRACKING AND OTHER ACID CATALYSED REACTIONS

Acid (and base) catalysis are involved in some of the oldest industrial reactions, such as hydrolysis of esters for soap manufacture and inversion of sugar cane. Friedel-Crafts reactions were discovered in 1877-1878 and aluminum chloride--a typical Friedel-Crafts type

---

<sup>x</sup> Data for these tables courtesy of Catalytica Associates, Inc.

TABLE A

MAJOR APPLICATIONS OF

HETEROGENEOUS CATALYSIS IN U.S. PETROLEUM

INDUSTRY

	<u>BBL/D</u>	<u>CAPACITY METRIC TONS/DAY</u>	<u>U. S. CATALYST SALES, MILLION LBS/YR</u>	<u>CATALYST VALUE MILLION \$/YEAR</u>
1) CAT. CRACKING	5,000,000	635,000	286	143
2) CAT. HYDROCRACKING	900,000	114,000	~ 2	20
3) NAPHTHA REFORMING	2,000,000	222,000	5	27
4) CAT. ALKYLATION	890,000	85,000	3,700	128
5) CAT. HYDROTREATING	2,000,000	260,000	22	45

TABLE B

MAJOR APPLICATIONS OF HETEROGENEOUS CATALYSISIN U.S. PETROCHEMICAL INDUSTRY

	<u>APPROXIMATE 1979 PRODUCTION (MILLION TONS/YR)</u>	<u>PRODUCT VALUE \$/YR IN MILLION \$</u>
1. <u>AMMONIA SYNTHESIS</u>	15	1,500
2. <u>METHANOL</u>	4.1	693
3. <u>STEAM REFORMING</u>	6.3 x 10 <sup>9</sup> SCFD	535
4. <u>OXIDATIONS</u>		
- Ethylene Oxide	2.5	1,600
- Formaldehyde	3.5	490
- Phthalic Anhydride	3.5	2,870
- Maleic Anhydride	0.2	200
5. <u>ACRYLONITRILE (AMMOXIDATION)</u>	1.0	560
6. <u>STYRENE (DEHYDROGENATION)</u>	3.8	2,660
7. <u>HYDROGENATIONS</u>		
- Aniline	0.3	274
- Cyclohexane	1.2	600
8. <u>VINYL CHLORIDE MONOMER (OXYCHLORINATION)</u>	3.5	1,050
9. <u>VINYL ACETATE MONOMER (OXYCHLORINATION)</u>	0.9	522
10. <u>BUTADIENE</u>	1.7	884

TABLE CMAJOR APPLICATIONS OF HETEROGENEOUS CATALYSTSIN COMMODITY CHEMICALS

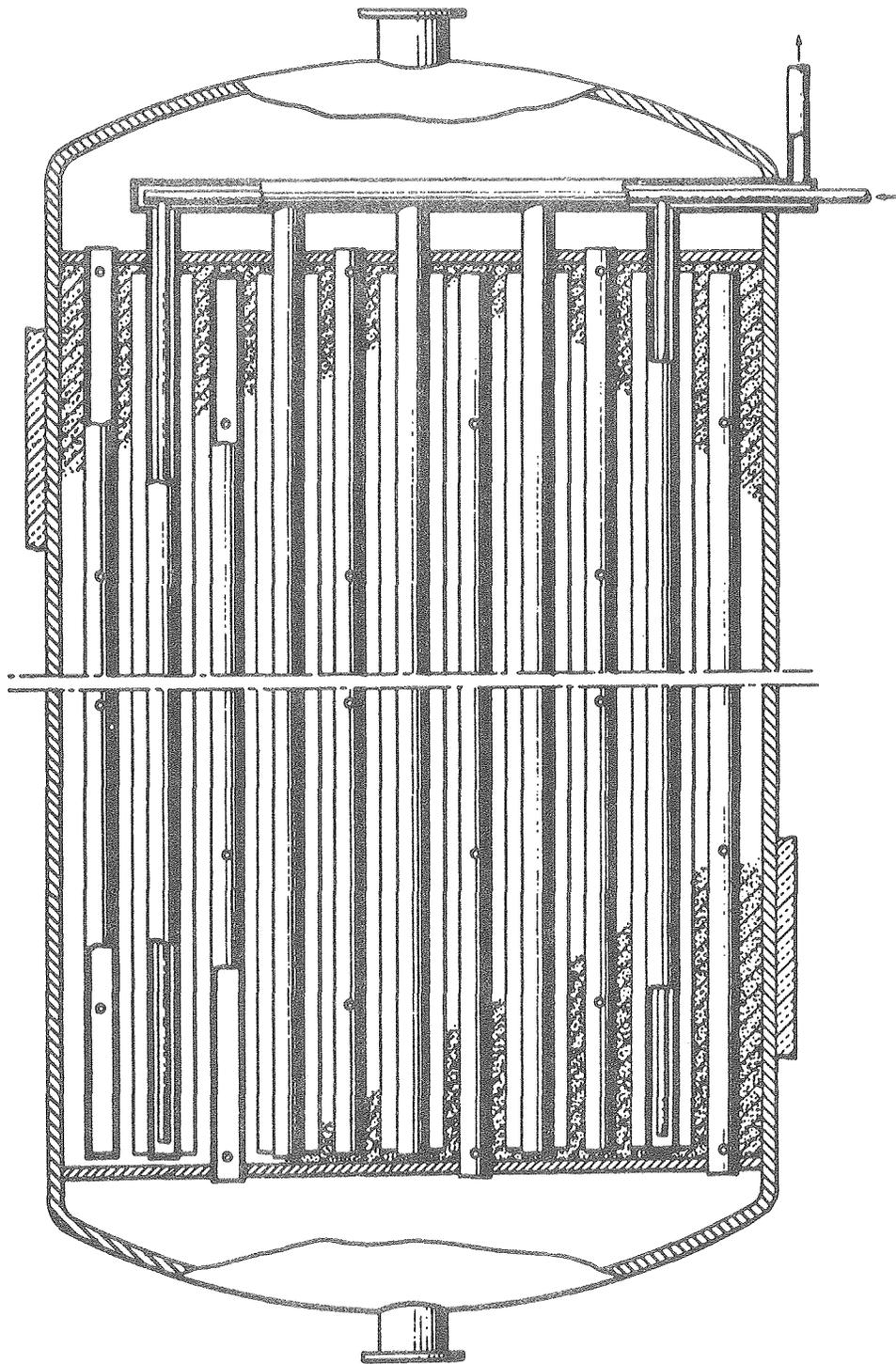
	<u>APPROXIMATE 1979 U. S. PRODUCTION (MILLION TONS/YR)</u>	<u>PRODUCT VALUE \$/YR IN MILLION</u>
1. <u>Sulfuric Acid</u>	40	1,800
2. <u>Nitric Acid</u>	8.5	\$2,040 (pure HNO <sub>3</sub> )



catalyst--was the first commercial catalyst used in converting heavier petroleum hydrocarbons to lighter fragments, particularly in the gasoline boiling range.

Gasoline (boiling between 38<sup>o</sup>C and 210<sup>o</sup>C and having a C<sub>4</sub> - C<sub>13</sub> range) comprises only about 15-25% of the natural petroleum. Most of this "straight run" gasoline consists of normal or slightly branched paraffins, some naphthenes, and a few aromatics, most of these components having low octane numbers. "Cracking" of heavier petroleum fractions over selective catalysts enhances the obtainable yield of gasoline from a barrel of crude oil and results in the formation of larger quantities of highly branched paraffins, olefins, and aromatics, all of which are high octane number components. The McAfee AlCl<sub>3</sub> process found limited application in the years following 1915, and was operated as a batch process with a severe problem in disposing of the sludges consisting of spent aluminum chloride dissolved in hydrocarbons. Gurwitsch<sup>( 2 )</sup> and Herbst<sup>( 3 )</sup> observed and detailed the catalytic activity of certain activated clays as early as 1912 and 1926, respectively. A major breakthrough occurred in 1936 after Eugene J. Houdry had solved a series of problems involving catalyst deactivation, regeneration, and stability, and overcame formidable engineering problems. It is interesting to note that Houdry was a mechanical engineer who was also an automobile race driver, and as such recognized that the limitations of the internal combustion engine at that time were not of a mechanical nature but lay in the constraints imposed by the low-octane number characteristics

of gasoline then available. In searching for a better gasoline, he studied the chemistry of hydrocarbons and the synthesis of branched chain paraffins and olefins, and of aromatics, by catalytic cracking of gas oils. Houdry devised a system of cyclic reaction and regeneration which maintained the cracking unit in heat balance, and which could be practiced commercially in a continuous mode. Cyclic operation of fixed-bed cracking units, utilizing the exothermic heat of regeneration to provide the required cracking temperatures (cracking is endothermic) became a reality when Houdry Process Corporation, together with Socony-Vacuum Oil Company and Sun Oil Company, built the first commercial units at plants of the two oil companies in 1936-1938, shortly before the outbreak of the Second World War. The catalyst was contained in numerous parallel tubes that were suspended in a molten salt heat exchanger, as shown in Figure 1. <sup>(4,5)</sup> Figure 2 shows a Houdry unit. In spite of the rapid refinements that followed, some of the original units were still in operation in the early 1960s. About 90% of the aviation gasoline base stock used in the battle of Britain came from Houdry Units.



XBL795-1560

Fig. 1. Houdry Catalytic Cracking Unit Reactor. Tubular catalyst containers in molten salt medium.

Figure taken from reference 4.

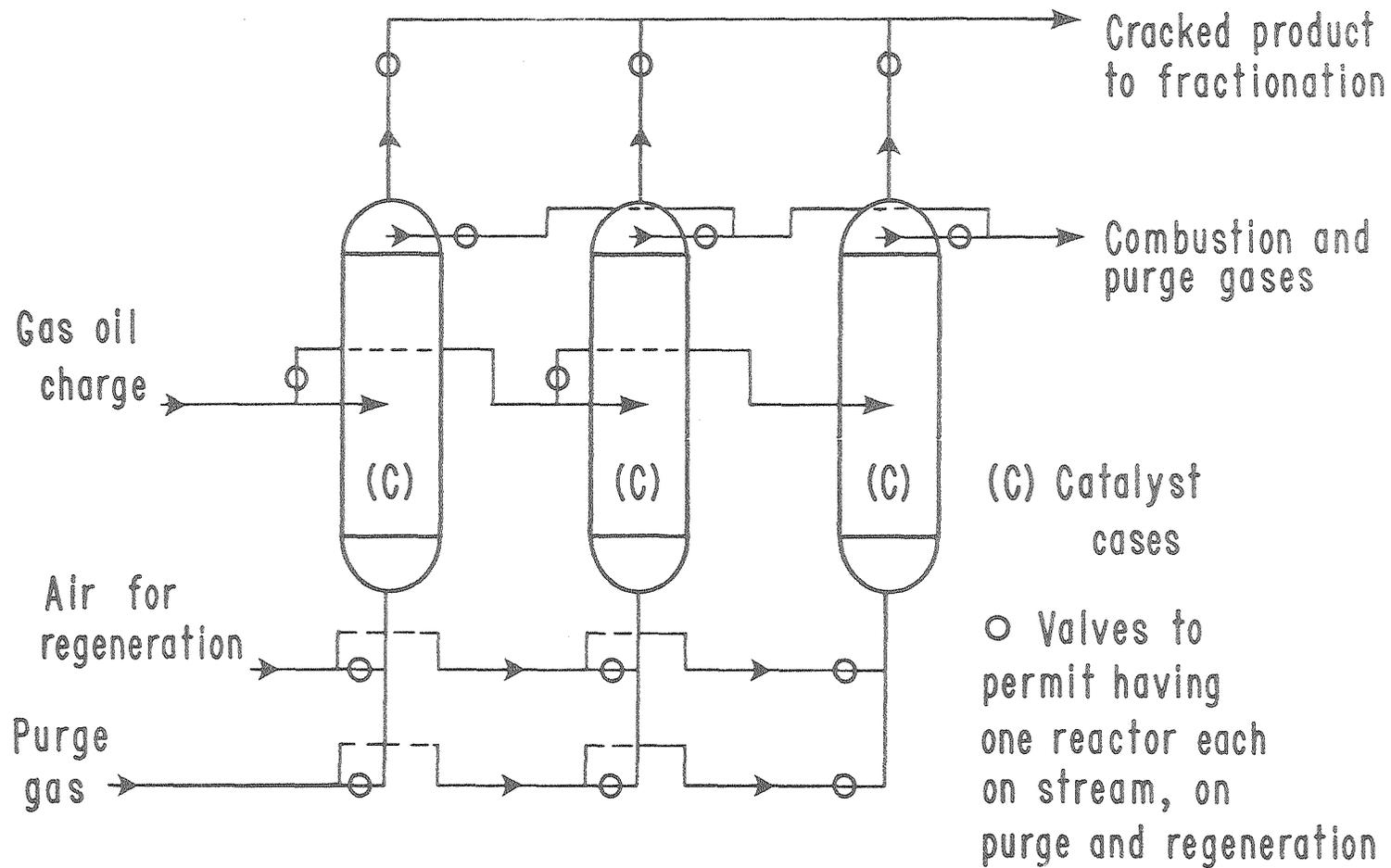


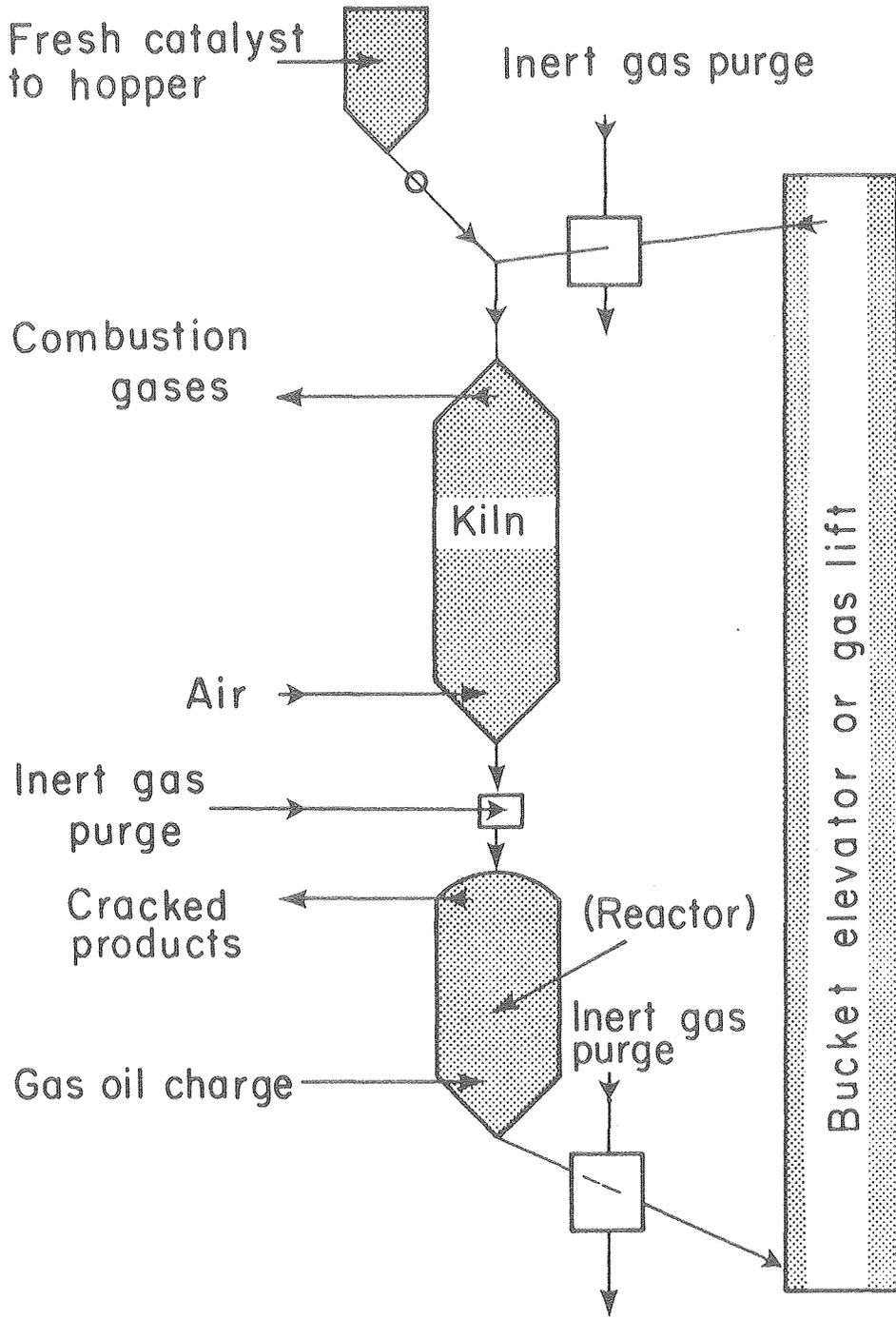
Figure 2 Schematic Drawing of Houdry Fixed Bed Catalytic Cracking Unit

XBL 798-2364

The sudden demand for large quantities of aviation gasoline during World War II accelerated the rapid expansion of the cracking process, and numerous units were built during the period from 1938 to 1950. At the same time, major improvements were made in the mechanical design of the cracking units and in the cracking catalyst.

The cyclic operation of the fixed bed units was replaced by designs which moved the catalyst continuously from a reactor through a purge zone to a regenerator, and from there through another inert gas-purge zone back to the reactor. This was accomplished by two quite different methods: In the moving-bed type of operation first introduced by Socony-Vacuum Oil Company in 1942<sup>(5)</sup>, the pelleted or extruded catalyst moved by gravity through reaction and regeneration zones, and was lifted from the bottom of one vessel to the top of the other by a bucket elevator (Figure 3). In the early 1950s, this design was further refined by replacing the elevator with a lift pipe in which the catalyst was blown by a high-velocity gas stream to the top vessel.<sup>(6)</sup> Similar designs were commercialized by Socony-Vacuum Oil Company under the name of "Thermoform Catalytic Cracking" (TCC), and by Houdry Process Corporation under the name of "Houdriflow." These units operated satisfactorily for many years, but are now gradually disappearing because their capacity is limited by heat-flow conditions. Units of larger than 20,000 bbl/day have not been built.

In 1941 a group of companies under the leadership of Standard Oil Company of New Jersey introduced the first "Fluidbed Catalytic Cracking Unit" (FCC).<sup>(5,7)</sup> In this revolutionary design, based largely on work by Lewis and Gilleland at M.I.T., the catalyst in the form of fine particles in the 30-200 mesh range was maintained in suspension in a stream of vaporized hydrocarbons, blown through the reactor and collected in a separator and in cyclones, passed through a stand-pipe in which it was purged to the bottom of the regenerator, and blown through the regenerator by an oxygen-containing gas stream and finally returned to the reactor (Figure 4). Over the years, many improvements--such as short-contact time and



XBL798-2365

Figure 3 Schematic Drawing of TCC Cracking Unit (Moving Bed)

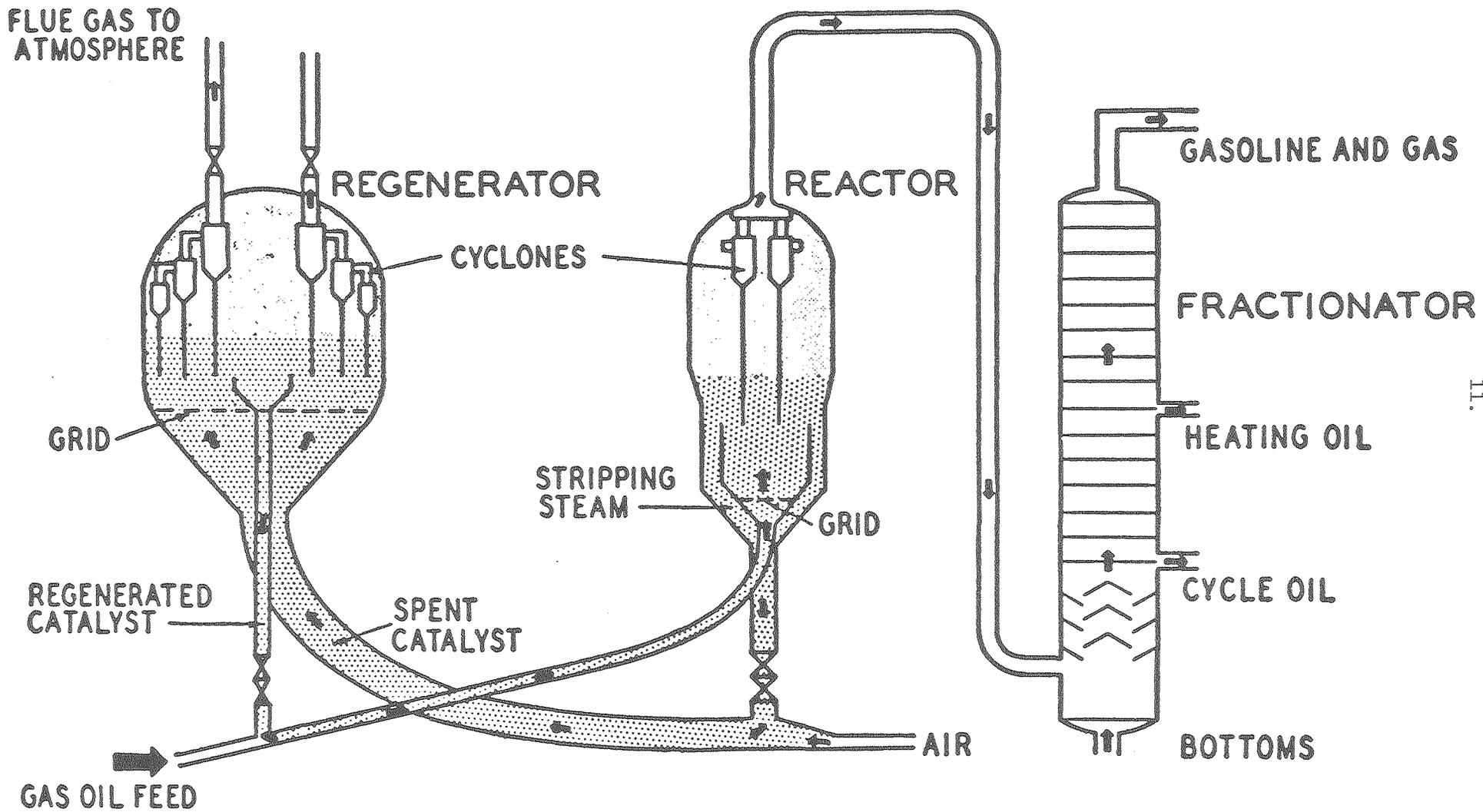
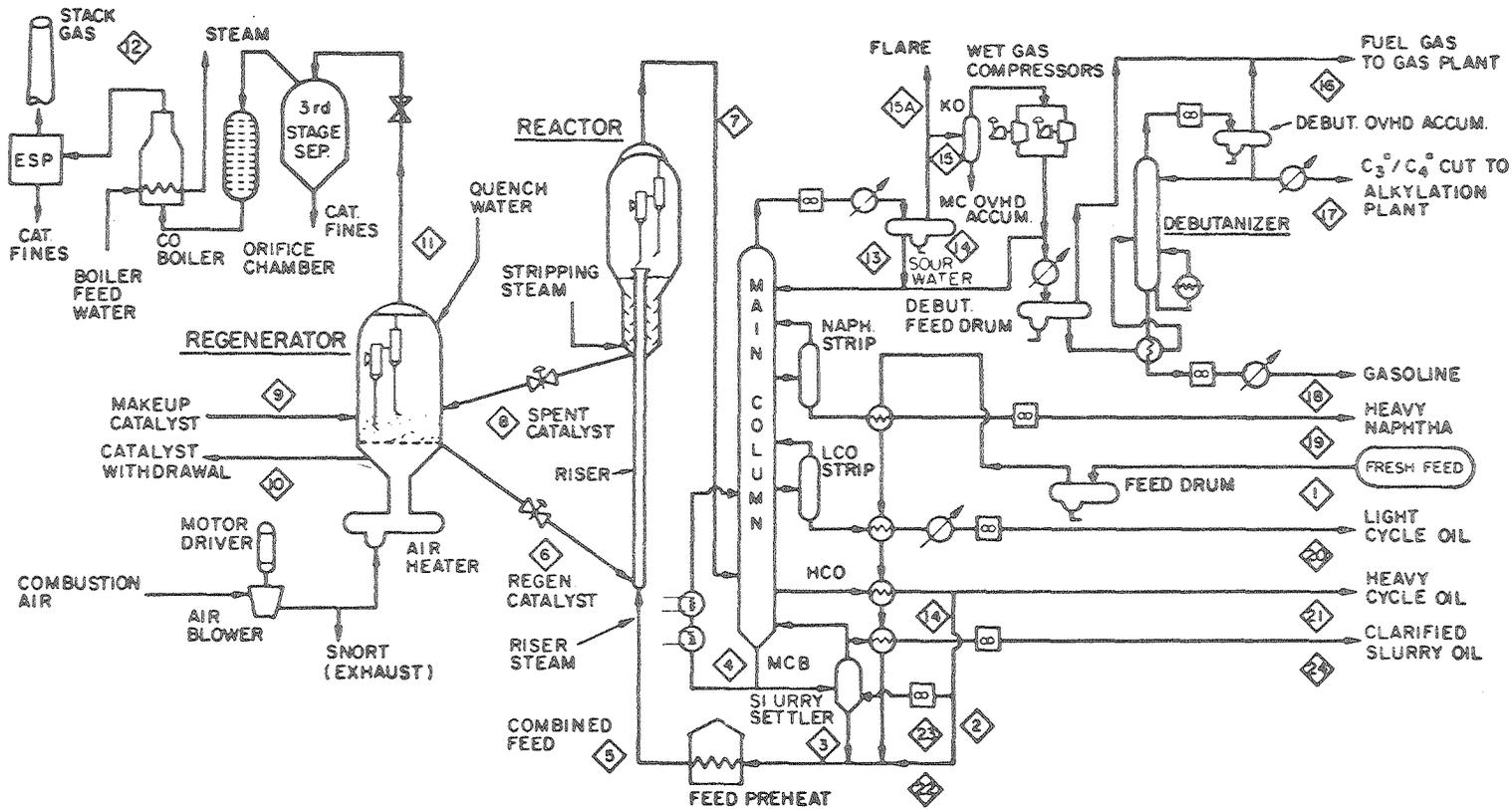


Fig. 4 Conceptual Fluid Bed Cracking Unit

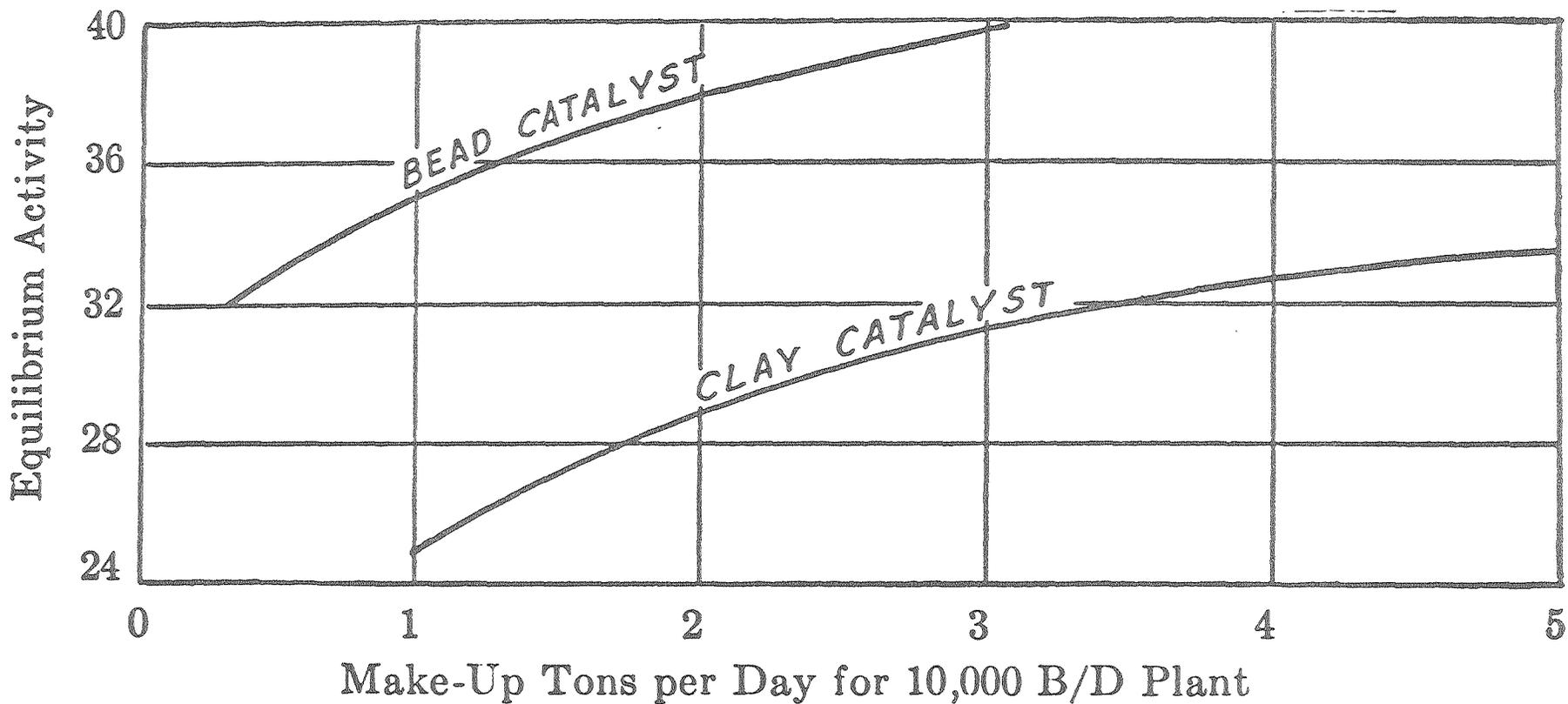
riser cracking--have been made in the engineering design of FCC units. ( 8 ) Riser cracking was made possible also by improvements in the physical strength of cracking catalysts. A modern short-contact time-fluid cracker is shown in Figure 5. (8) The FCC design could be scaled to very large units because of the rapid heat exchange between carrier gas and catalyst, which permits very close temperature control. The vast majority of present cracking units are of the FCC type, and the fluid-bed technology has been applied to other processes, particularly those of a highly exothermic or endothermic nature. In 1978 the U.S. catalytic cracking capacity was about 5,000,000 bbl/day.

While these design changes were taking place, improvements were made in the catalyst type and composition. The original cracking catalysts were acid-treated clays of the montmorillonite type. They permitted larger yields of gasoline of higher octane number than had previously been obtainable by thermal cracking of gas oils. The clays were gradually replaced by amorphous synthetic silica-alumina catalysts which were more stable under regeneration conditions and also gave a better product distribution. ( 9 ) Gasoline yields obtainable from gas oil increased from about 20 percent by thermal cracking to over 40 percent with silica-alumina catalysts. The importance of the catalyst shape and pore distribution was recognized about 1945. Bead catalysts were invented by Marisic at Socony-Vacuum and resulted in lower attrition losses than pelleted or extruded catalysts in TCC-type units. The attrition and activity advances of bead versus extruded-clay catalysts is shown in Figure 6. (4) Open structure beads, produced by incorporating crystalline alumina during gelling, increased activity and reduced diffusion limitations. Variations of the silica/alumina ratio (normally 65/35) permitted fine tuning of product yields. Silica-magnesia catalysts were introduced in 1952 and resulted in better gasoline yields (but of slightly lower octane number). However, these catalysts never reached large-scale use because of regeneration problems. ( 10 ).



XBL 795-9542

Fig. 5 Modern F.C.C. Unit  
Figure taken from Reference 8.



XBL 793-8900

Fig. 6 Activity and Make-up Rate of Clay and Silica-alumina Bead Catalysts  
Figure taken from Reference 4.

Silica-alumina catalysts were used in FCC units as well as in TCC units, but because of the small particle size used in FCC did not require the attention to diffusional problems encountered in TCC-type units. The whole area of FCC cracking has been reviewed in detail by Venuto and Habib. ( 8 )

A major revolution in cracking catalysts occurred in the early 1960s, and this will be described in the section on "zeolite catalysis." (III)

Leaving catalytic cracking temporarily, there are a series of other acid catalysed reactions which have become important, mostly in the fuel area. These include polymerization of olefins to dimers, trimers, and tetramers; alkylation; and isomerizations of paraffins and aromatics. All of these have been previously described in the literature, ( 11 ) and no breakthroughs have occurred in polymerization of  $C_3$  and  $C_4$  hydrocarbons to fuels in the last 30 years although a number of refinements have been introduced.

In alkylation to high-octane gasoline, both the sulfuric-acid and hydrofluoric-acid processes continue to dominate the field. ( 12 )

Addition of an olefinic hydrocarbon to another molecule is being practiced in two major areas: (1) in the alkylation of isobutane with butenes or propene to produce highly branched  $C_7$  and  $C_8$  hydrocarbons as high octane number gasoline components; (2) in the alkylation of aromatics with ethylene or propene to produce alkyl-

aromatics. Paraffin alkylation was discovered by V. N. Ipatieff in 1935 and commercialized in 1942. The two catalysts in commercial use are sulfuric acid and hydrofluoric acid. Alkylation supplied large volumes of aviation gasoline in World War II. The subject has been reviewed by R. M. Kennedy<sup>( 11 )</sup> and others and improvements in the process technology since then do not involve major inventions.

Alkylation of aromatics with olefins is used primarily in the production of ethylbenzene and of cumene. Anhydrous  $\text{AlCl}_3 + \text{HCl}$  catalysts have been used since the early 1940ties. A major improvement in catalyst technology was introduced in 1977 by the use of zeolites and will be discussed in the section on zeolites. It has eliminated the problems of acid sludge erosion.

In aromatics alkylation and aromatics isomerization, novel process technology has emerged which will also be described in the section on zeolites.

The need for paraffin isomerization arose during World War II. Alkylation was one of the few routes to high-octane-number aviation gasoline. While sufficient amounts of  $\text{C}_4$  olefins were available from catalytic and thermal cracking, there was a shortage of isobutane. On the other hand, there were supplies of n-butane which could be isomerized. Two routes, commercialized by Shell Oil Company and Texaco in 1941 were used for isomerization of normal to isobutane. Both were based on aluminum chloride as a catalyst and gaseous HCl as a promoter.<sup>( 13 )</sup> Over 40 units were built. In one process, a

sludge of  $\text{AlCl}_3$  in aromatic hydrocarbons served as a catalytic liquid through which the n-butane gas was passed; in the other, anhydrous  $\text{AlCl}_3$  was deposited on alumina or on bauxite, and the process was operated in a fixed-bed configuration. The major problem with both processes was the highly corrosive nature of the sludge or of the sludge drippings from the solid catalyst. Frequent reactor replacement was required. Paraffin isomerization, previously dependent on  $\text{AlCl}_3$ -type catalysis, has since then made progress by the introduction of dual functional catalysts, described in another section.<sup>(10)</sup> The newer processes have concentrated on  $\text{C}_5$  rather than  $\text{C}_4$  hydrocarbons.

### III ZEOLITE CATALYSIS

Crystalline alumino silicates possessing base exchange properties have been known for well over 100 years and occur quite frequently in nature. They have found early application in ion-exchange chemistry, but their catalytic usefulness was discovered only in the late 1950s. Early attempts to use them as a base for catalytic cracking failed, and for a long time it was believed that the regular and uniform pore structure of a crystalline material was inferior to the pore-size distribution of amorphous catalysts. In the mid-1950s Union Carbide Corporation first commercially produced synthetic zeolites of the x and y type (faujasites) as adsorbents; (Fig 7.) they later became ingredients of zeolite catalysis. While Rabo et al. pointed out in 1960<sup>(14)</sup> that these materials possessed activity for such reactions as isomerization, it remained for Plank and Rosinsky at Socony-Mobil Oil Corporation to stabilize zeolites x and y so that they could withstand regeneration temperatures and steam partial pressures occurring in cracking without sintering and losing crystallinity. They achieved this by ion exchanging rare earth metals for alkali metals, and using a matrix of silica-alumina<sup>(15,16)</sup> to separate zeolite crystallites.

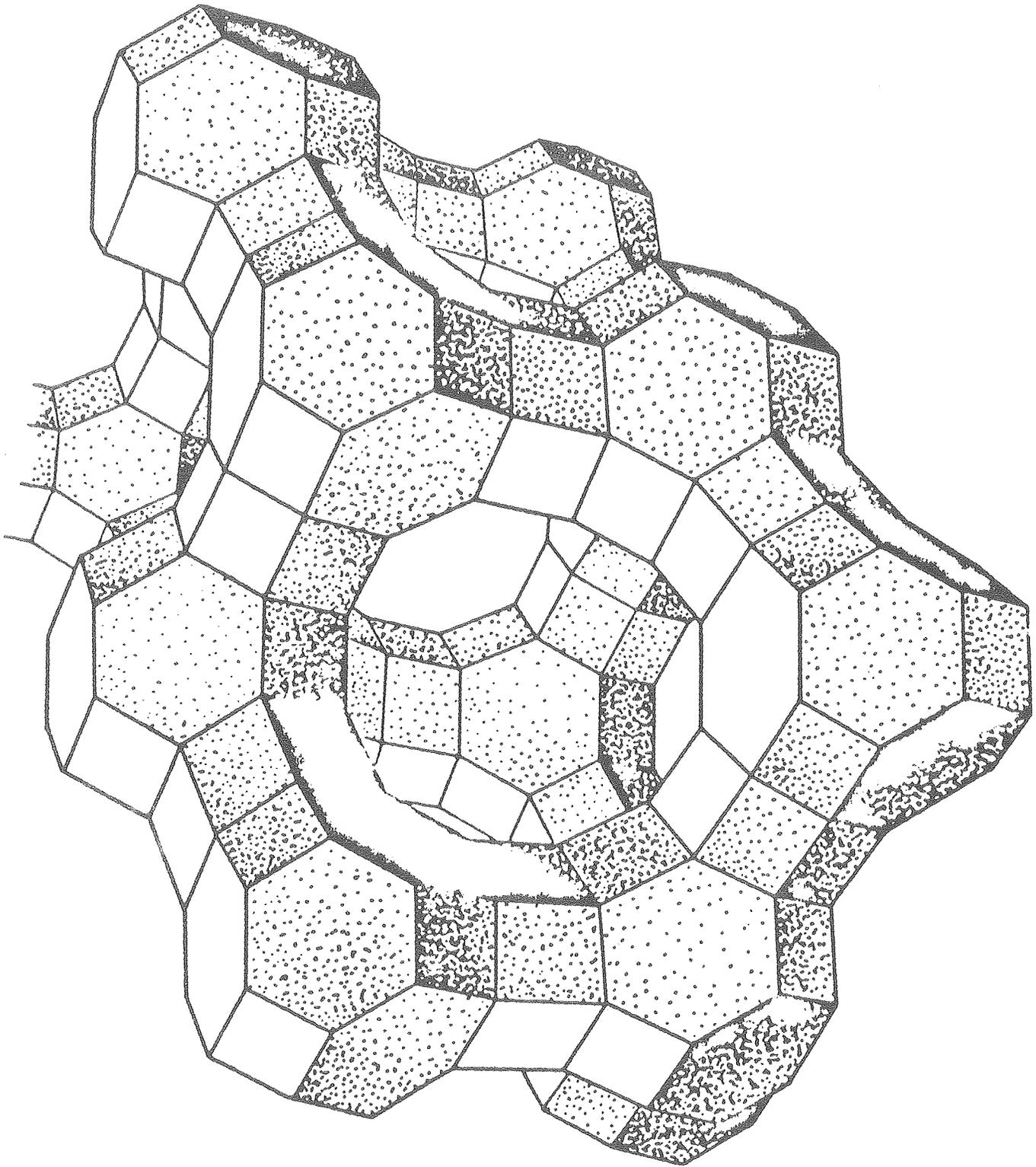
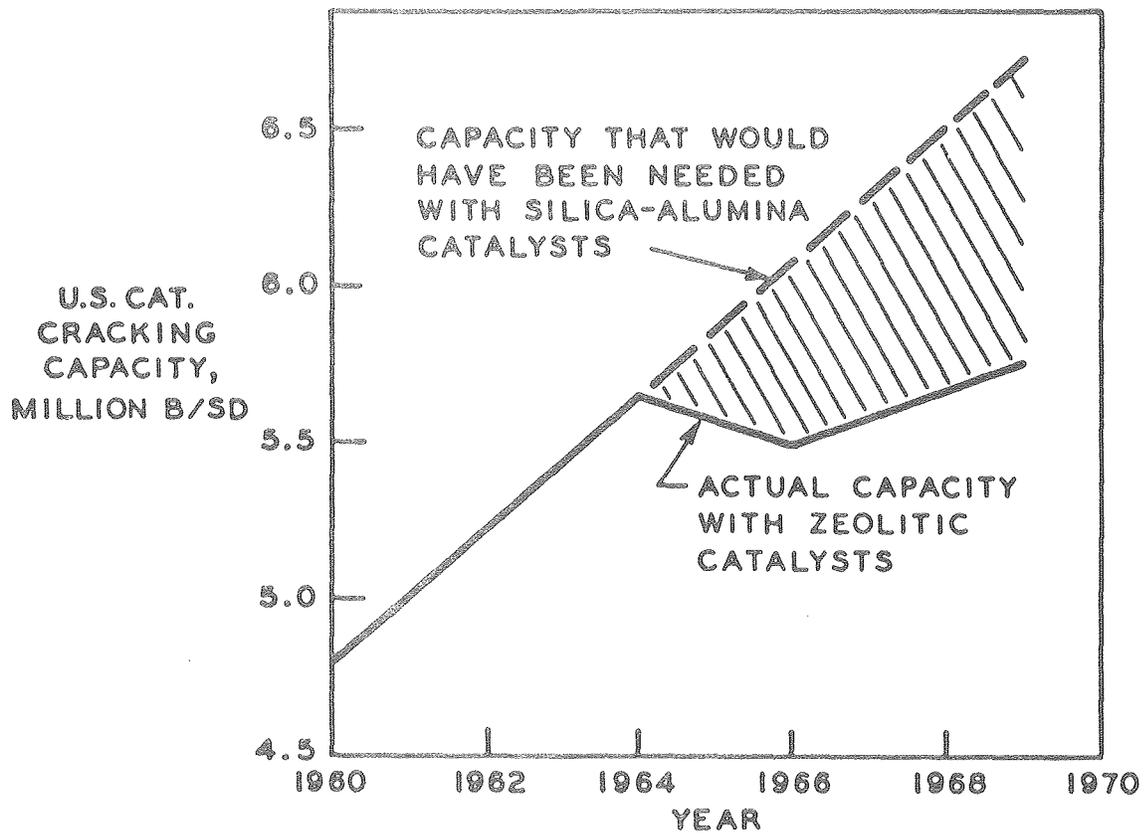


Fig. 7. Faujasite Zeolite

The new zeolite-cracking catalysts exhibited greater activity and selectivity than all previous catalysts (Tables 2 and 3). While their initial introduction was for use in TCC units in late 1961, fluid-bed zeolite catalysts were soon manufactured and used. The great selectivity of these catalysts sharply reduced the amount of gas oil required to produce gasoline. Figure 8 shows the U.S. catalytic cracking capacity as a function of time. The sudden change of slope in the years between 1964 and 1970 is due to the fact that the capacity of existing units was increased by the use of zeolite catalysts to such an extent that the steadily increasing demand for gasoline could be met for several years without new capacity. It has been estimated that savings of crude oil alone by this improved selectivity amounted to about \$200 million per year, prior to the quadrupling of oil prices in 1974. No history of industrial catalysis would be complete without mention of the patent litigation that ensued for more than ten years and ended with upholding the validity of the Plank and Rosinsky patents. About 90 percent of all catalytic cracking today employs zeolite catalysts. About 290 million pounds of cracking catalyst with a value of \$145 million were produced in 1978. <sup>(17)</sup>

A series of catalyst improvements followed the initial introduction of zeolites, each adding to stability or selectivity of the catalyst. <sup>(18)</sup> In 1977, a new series of catalysts came on the market which contained, in addition to the zeolite, a combustion promoter. This permitted catalyst regeneration to very low residual coke levels at relatively low regeneration temperatures, and also permitted oxidation of CO to CO<sub>2</sub>, reducing pollution and heat-loss problems. These catalysts, again developed by Mobil Oil, contain extremely small amounts (0.01-50 ppm) of platinum impregnated on the catalyst or introduced with the feed stock. <sup>(17)</sup> The role of oxidation promoters was well-known. But many previous attempts to incorporate them into cracking catalysts failed, because the oxidation component

### EFFECT OF ZEOLITIC CATALYSTS ON CATALYTIC CRACKING CAPACITY



XBL 793-9016

Figure 8

Table 2<sup>(15)</sup>

Comparison of Gasoline Compositions from Gas Oil  
Cracking Catalysed by Silica-Alumina  
and Zeolite

Feed:	Calif. virgin gas-oil		Calif. coker gas-oil		Gachsaran gas-oil	
	5	1	5	1	5	1
Catalyst, durabead gasoline						
% Paraffins	21.0	8.7	21.8	12.0	31.9	21.2
% Cycloparaffins	19.3	10.4	13.4	9.5	14.3	15.7
% Olefins	14.6	43.7	19.0	42.8	16.3	30.2
% Aromatics	45.0	37.3	45.9	35.8	37.4	33.1

Durabead 1 = silica-alumina

Durabead 5 = early generation zeolite (REHX)

Table 3<sup>(15)</sup>

Yields of Products from Cycle Stocks Cracked Over  
Durabead 5 and Durabead 7 Compared with Si/Al

	Si/Al Yields	Durabead 5 <sup>1</sup>		Durabead 7 <sup>2</sup>	
		Yields	Delta Si/Al	Yields	Delta Si/Al
Augusta catalytic light fuel oil <sup>3</sup>					
Conversion, Vol %	35.6	35.6	-	35.6	-
C <sub>5</sub> + gasoline, Vol %	22.1	25.9	+3.8	29.2	+7.1
Total C <sub>4</sub> 's, Vol %	8.7	7.9	-0.8	6.2	-2.5
Dry gas, Wt %	5.2	4.1	-1.1	3.5	-1.8
Coke, Wt %	4.3	2.2	-2.1	1.4	-2.9
Beaumont heavy catalytic fuel oil <sup>4</sup>					
Conversion, Vol %	42.5	42.5	-	42.5	-
C <sub>5</sub> + gasoline, Vol %	24.5	26.3	+1.8	30.6	+6.1
Total C <sub>4</sub> 's, Vol %	9.4	9.4	0	8.2	-1.2
Dry gas, Wt %	6.5	5.2	-1.0	4.7	-1.5
Coke, Wt %	8.7	7.8	-0.9	4.9	-3.8

<sup>1</sup>Contains REHX in silica-alumina.

<sup>2</sup>Contains REHY in silica-alumina.

<sup>3</sup>Properties—27.3°API, Aniline No. = 139.5°F, (59.8°C), ASTM boiling range = 516°-666°F. (269-353°C).

<sup>4</sup>Properties—19.5°API, Aniline No. = 157.5°F, (69.8°C) ASTM boiling range = 410°-760°F. (210-405°C).

acted also as a dehydrogenation component during cracking, and resulted in undesirably large yields of hydrogen. No such effect has been observed with the new catalysts. One must marvel, however, at the turnover rates these tiny amounts of precious metal must achieve during regeneration. It raises the old question of how much of the surface of catalysts is active in a catalytic reaction.

The introduction of a zeolite-cracking component into hydrocracking catalysts will be discussed in the section on dual functional catalysis.<sup>(10)</sup> This was commercialized by Chevron and Union Oil Company of California about 1970.

Almost simultaneously with the introduction of zeolite-cracking catalysts came the discovery of catalytic shape selectivity by P. B. Weisz and his co-workers at Mobil.<sup>(19)</sup> They stipulated and demonstrated that diffusional constraints prevented the entry of molecules above certain dimensions into the pores of certain zeolites, and introduced the concept of "molecular engineering." The first process based on this concept was disclosed in 1968 and was called "Selectoforming."<sup>(20)</sup> The catalyst used was a naturally occurring zeolite with about 5 $\text{\AA}$  pore openings (contrasting the 9-12  $\text{\AA}$  openings of faujasites and the 3 $\text{\AA}$  of zeolite A). When a catalytic reformat was passed over this catalyst containing a small amount of nickel as a hydrogenation component in the presence of hydrogen, a selective cracking of n-paraffins occurred while branched chain hydrocarbons and aromatics passed undisturbed. This resulted in the removal of the lowest octane number components of gasoline, converting them mostly to LPG hydrocarbons.

Since 1974, a series of novel processes was introduced by Mobil Oil based on the unique properties of a synthetic zeolite called ZSM-5.<sup>(21)</sup> (Fig. 9). This material has pore openings of 5-7 $\text{\AA}$  and exhibits shape selectivity, acid activity, and an unusual resistance to coking. It extended the range of "Selectoforming" by cracking both normal and singly branched paraffins, but not the high-octane

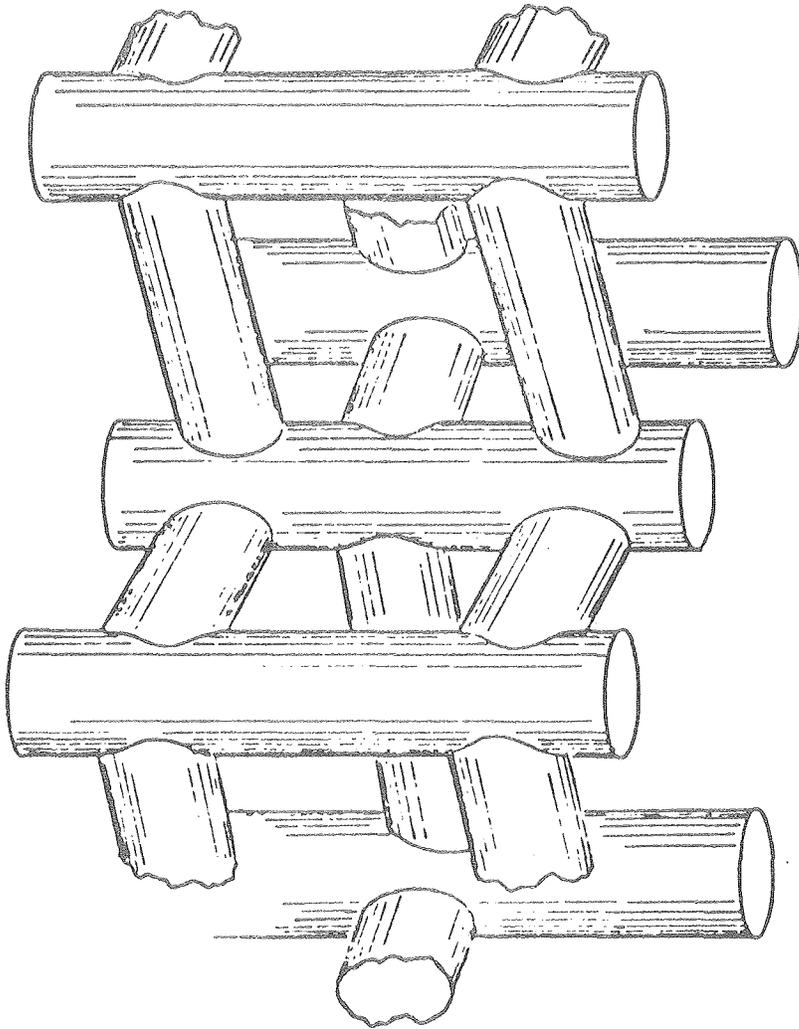


Fig. 9. Pore Arrangement of ZSM-5 Zeolite

number hydrocarbons possessing a quaternary C atom. In addition, it permitted simultaneous alkylation of simple aromatics like benzene with the olefinic fragments from paraffin cracking, resulting in higher liquid yields. ( 22 ) The "M-forming" process was first operated in Germany in 1976.

Shape selective cracking also is the basic reaction of the "Mobil Distillate Dewaxing" (MDDW) process. ( 23 ) This process was first tested in a commercial installation in France in 1974 and has been operating in a number of refineries in various parts of the world since 1978. It serves two purposes: one is lowering the pour point of middle distillate fractions such as diesel and heating oils to make them suitable for cold-weather operations, the other is permitting the inclusion of higher boiling material in these fractions to increase their yield-per-barrel of crude oil. In both cases, the pour point reduction is achieved by cracking waxy normal paraffins selectively with a relatively small yield loss. The cracked product consists largely of gasoline of good octane number. The reaction is carried out over ZSM-5-type zeolite in the presence of hydrogen, but there is essentially no hydrogen consumption. Catalyst deactivation is gradual and can be reversed by a hydrogen purge, indicating that it occurs probably by sorption of nitrogen compounds on the catalyst.

In another section (dual functional catalysis), mention will be made of xylene isomerization. ZSM-5-type catalysts have largely replaced Pt-Al<sub>2</sub>O<sub>3</sub> in this application. They isomerize the three xylenes to equilibrium. Ethylbenzene is largely disproportionated eliminating the need for fractionation to remove ethylbenzene from the feed. Catalyst life in this application has exceeded two years. Recent patents indicate that chemical modification of ZSM-5 with phosphorous or carbon can further increase selectivity and result in p-xylene yields far exceeding equilibrium.

The same type of catalyst can replace  $\text{AlCl}_3$  in the alkylation of benzene with ethylene to produce ethylbenzene. <sup>(21)</sup> This eliminates catalyst disposal problems and substitutes a fixed-bed reactor system for a sparged tower.

Toluene disproportionation to benzene and xylenes is another commercial process operated with the ZSM-5 class of catalysts.

The latest application of this type of catalyst--which has not yet become commercial although it has been in operation in a sizeable pilot plant--is conversion of methanol to high-octane gasoline. <sup>(24)</sup> This new chemical reaction involves an internal dehydration and polymerization with simultaneous isomerization and hydrogen transfer. Methanol goes via dimethylether to an olefinic entity, which then forms isoparaffins and aromatics. The catalyst is ZSM-5 and operation can be in either fixed or fluid bed at quite mild conditions. The importance of the reaction lies in the possibility of converting either coal or natural gas via methanol (a well-established old technology) to gasoline. Several reaction mechanisms have been suggested for this reaction that had not been previously observed. It is not limited to methanol, but works with higher alcohols, ethers, and other oxygenates. The yields are stoichiometric, in the case of methanol giving 44 percent hydrocarbons and 56 percent water. The reaction is highly exothermic and heat removal is the major engineering process problem. Variations in operating conditions permit changes in the aromatics/paraffin ratio, and allow relatively high yields of ethylene and propylene.

IV DUAL FUNCTIONAL CATALYSISa) Naphtha Reforming

Catalytic reforming of naphthas serves to improve the octane number of gasoline by isomerizing paraffins, dehydrogenating cyclohexanes, dehydroisomerizing methylcyclopentanes, aromatizing some paraffins and also hydrocracking some paraffins.

The reforming of straight-run naphthas to achieve production of high-octane number gasolines developed slowly from thermal reforming ( 25 ) to conversion over molybdena-alumina catalysts at elevated pressures

and in the presence of hydrogen. This process was used during World War II to produce toluene from methylcyclohexane. A continuous fluid bed process commercialized by Standard Oil of Indiana never achieved broad application after an explosion destroyed the first commercial plant in 1947, demonstrating the hazards of operating high-pressure hydrogenative processes in a continuous mode. About 1950 a new generation of reforming processes were introduced. "Platforming," the most successful of them, was developed by Universal Oil Products Company (UOP) and was also first on the market, closely followed by "Catforming" (Atlantic Refining Company) and "Houdriforming" (Houdry Process Corporation). All three processes employed a platinum catalyst on an acidic base. In "Platforming" and "Houdriforming," 0.3-0.8% Pt was supported on  $\gamma$ -alumina, and high activity levels were maintained by adding very small amounts of a hydrogen halide or hydrogen halide precursor to the feed. In "Catforming," the catalyst support consisted of a silica-alumina gel. All three processes operated at 400-600 psig (27-40 at) in the presence of hydrogen, and at 800-950 °F. (430-510°C) Life cycles were long and activity was maintained by gradually raising the temperature of operation to balance catalyst deactivation. After six to twelve months of operation, the catalyst was replaced by a fresh batch and the platinum of the spent catalyst was recovered by solution chemistry. Somewhat later it was learned that these catalysts could be regenerated by careful oxidation. The major improvements achieved by these catalysts were the ability to isomerize paraffins to highly branched entities, dehydrogenate naphthenes to aromatics, dehydroisomerize methylcyclopentanes to aromatics, and convert some paraffins to aromatics by dehydrocyclization. In the course of naphtha reforming, hydrogen is produced as another product, and this reformer hydrogen supplies a large percentage of refinery demand for hydrogen. The dual functional nature of reforming catalysts, possessing hydrogenative-dehydrogenative function as well as acidic properties, was described in 1953 by Mills, Heinemann, Milliken, and Oblad<sup>(26)</sup> and is illustrated in Figure 10.

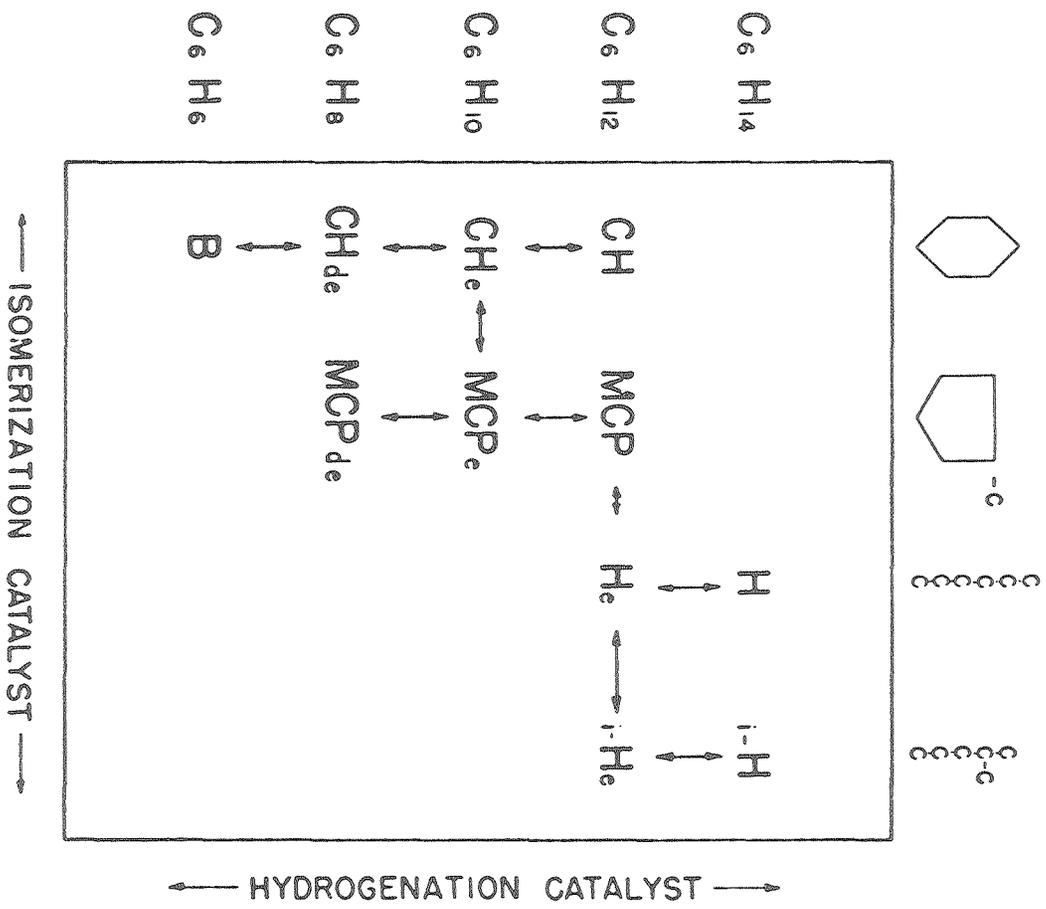


Fig.10. Dual Functional Reforming  
Figure taken from reference 26.

XBL 793-9019

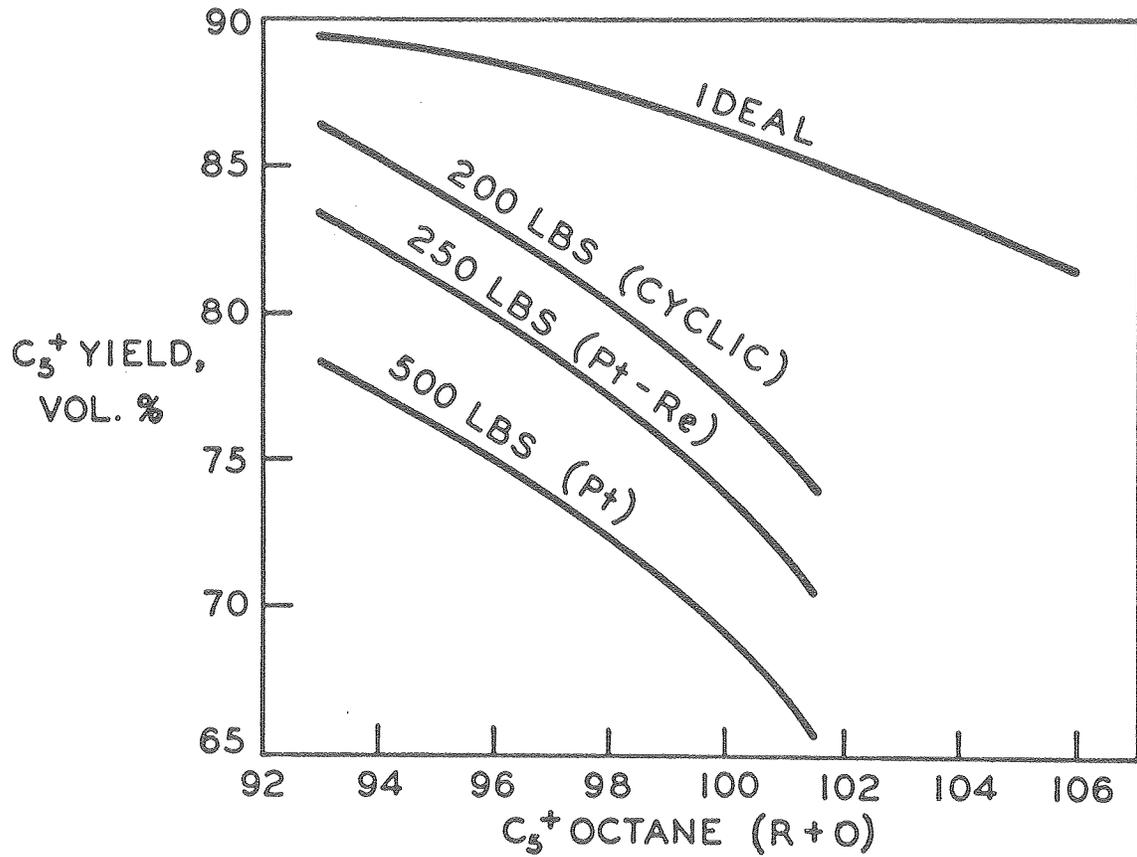
Their stipulation of the intermediary role of olefinic entities in the reaction mechanism was confirmed by P. B. Weisz and C. D. Prater in 1956, <sup>(27)</sup> who showed the presence of these olefins in the small amounts permitted by equilibrium considerations.

Since aromatics have very high octane numbers (> 100) and can be tolerated in gasoline up to almost 50vol%, it was soon recognized that a high degree of aromatization was desirable and would proceed best at lower pressures. Figure 11 indicates the yield at various octane numbers at different pressures. Since catalyst deactivation increases as pressure is lowered, utilization of this concept required more stable and regenerative catalysts. It was found in 1953 that eta-alumina was a more stable and active base; and in 1954 Standard Oil of Indiana introduced "Ultraforming," followed in 1956 by Esso's "Powerforming." These latter processes employ a cyclic mode of regeneration. Because of the relative ease of regeneration, the reforming can be operated at lower pressures; this permits better aromatization and higher octane number at the expense of more rapid catalyst deactivation.

All reforming processes use a multireactor system (usually three reactors, see Figure 12. <sup>(28)</sup> The first two reactors are endothermic because the major reaction in these is dehydrogenation; and the third reactor is exothermic because of hydrocracking and hydrogenation. Interstage heaters are employed to permit the same temperature at each reactor inlet. The last reactor operates at the highest average temperature and shows the most rapid aging. In the cyclic processes there is a spare reactor which undergoes regeneration, after which it is substituted for the first reactor, which becomes Number 2. The second reactor becomes Number 3, and the third is withdrawn and regenerated.

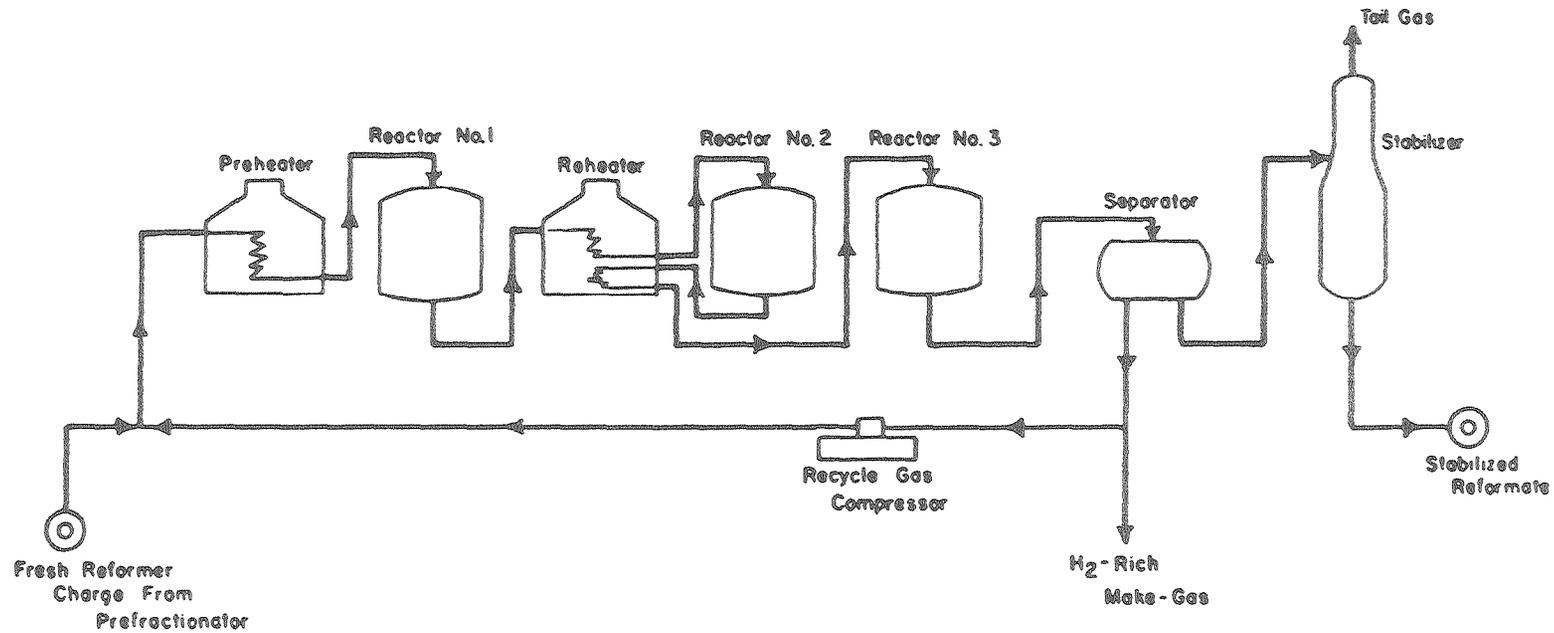
In the case of naphtha reforming, just as in catalytic cracking, the original process development involved the engineering design of a new unit concept as well as catalyst development.

YIELD VS. OCTANE FOR REFORMING  
OF C<sub>6</sub>-360 MID-CONTINENT NAPHTHA



XBL 793-9017

Figure 11



XBL 793-8901

Fig. 12. Catalytic Reforming Unit

In both cracking and reforming, further impressive improvements were achieved by catalyst modifications that permitted use of the new catalysts in existing units. In a period of high investment-and-construction costs, this reduced the risk of introducing new process technology--a risk that might otherwise have been unacceptable. A major step forward in the art of naphtha reforming occurred in 1967 with the introduction of catalysts containing, in addition to platinum, another metal (or metal oxide) on an alumina base. Chevron's "Rheniforming" process<sup>(29)</sup> was first on the market. This catalyst, containing rhenium in addition to platinum, provides greater stability. In 1975 Exxon commercialized operation with another catalyst, said to contain iridium and platinum and providing stable operation at quite low pressure. Sulfur sensitivity is greater than that for Pt catalysts. About 5 million pounds of reforming catalysts worth \$28 million were sold in 1978.<sup>(17)</sup>

Bimetallic catalysis is based on research on the concept of bimetallic cluster catalysts. Such catalysts consist of metallic clusters composed of atoms of two or more different metals in a state of high dispersion on a carrier.<sup>(30)</sup> The impact of this research, while already apparent in catalytic reforming as outlined above, is likely to increase over the next few years. Isomerization, hydrocracking, and hydrogenation will be affected. Vinylacetate manufacture with palladium-gold catalysts,<sup>(31)</sup> and olefin partial oxidation (see section on oxidation) with silver-gold or copper-gold catalysts,<sup>(32)</sup> are in the offing.

#### b) Isomerization

Catalysts used for isomerization are almost identical with those used in reforming. This is natural since isomerization is one of the important functions of reforming. Of the several processes developed, the Shell and UOP C<sub>5</sub> isomerization processes have, since

the late 1950s, replaced  $\text{AlCl}_3$  catalysis. In the case of aromatics isomerization, one is primarily concerned with xylene isomerization. In this case, p-xylene is removed (e.g., by fractional crystallization) from a mixture of xylenes. The remaining o- and m-xylene rich mixture is isomerized to equilibrium and the p-xylene again removed, recycling the remainder. Atlantic Refining Company's "Octafining" process using  $\text{Pt-Al}_2\text{O}_3$  or  $\text{Pt-SiO}_2\text{-Al}_2\text{O}_3$  catalyst was introduced in 1960 by Mitsui and has found broad application as p-xylene demand for dacron fabrics mushroomed. <sup>(33)</sup> It operates in the presence of hydrogen at about  $400\text{-}500^\circ\text{F}$  ( $205\text{-}260^\circ\text{C}$ ) and  $150\text{-}350$  psig, (10-23 at) and the catalytic mechanism is similar to the one involved in reforming. Imperial Chemical Industries (ICI) has commercialized another process that employs silica-alumina cracking catalysts at  $400\text{-}500^\circ\text{C}$  and atmospheric pressure in the absence of hydrogen. This process requires frequent catalyst regeneration (every second or third day), while the "Octafining" process operates on the same catalyst charge for six to twelve months, without regeneration.

In 1976 Mobil Oil Corporation introduced the "Mobil Vapor Phase Isomerization Process" (MVPI) and in 1978 the "Mobil Low Pressure Isomerization Process" (MLPI), each employing zeolite catalysts. These have been discussed in the section on zeolites. The MVPI process has conquered about three-fourths of the free-world's  $\text{C}_8$  isomerization capacity. It is not a dual functional catalyst, nor is the ICI catalyst.

### c) Hydrocracking

Hydrocracking has assumed increasing importance as feedstocks for fuels became heavier and supplies of gas oil for catalytic cracking and of naphtha for reforming became insufficient to supply the gasoline market. The relatively high carbon/hydrogen ratio of high-boiling fuels and their aromaticity made them unsuitable as cracking feedstocks, at least without prior hydrogenation. Conversion of heavier gas oils by hydrogenative processing dates back to pre-World War II technology

developed by M. Pier and his associates at I.G. Farben Industrie in Germany between 1925 and 1930, in collaboration with Standard Oil of New Jersey, operating at pressures of 3000-5000 psig. (200-333 at). The combination of hydrogenative and acid functions in catalysts to convert heavy petroleum fractions to gasoline and dry gas under high hydrogen partial pressure, however, did not become a large-scale commercial reality until the 1960s. This was primarily because long catalyst life was required for a process operating at high pressure (with the time-consuming and costly requirement to depressure, purge, and after regeneration to purge and repressure again), and also because nitrogen compounds in the feed tended to rapidly deactivate the cracking function. About 1960, catalysts and systems were found that operated at lower pressures (2000 psig).

Union Oil Company (together with Esso) and Chevron Oil Company pioneered hydrocracking processes using nickel or nickel-tungsten on silica-alumina as catalysts. <sup>(34)</sup> In later versions, zeolites of the fanjasite type were substituted for the silica-alumina base in about 1966-1967. With feeds having high nitrogen compound content, a two-reactor system was used in which the nitrogen compounds were converted in a first hydrogenation reactor to ammonia over nickel-tungsten or tungsten sulfide on alumina or silica with, of course, concomitant hydrogenation of some aromatics. Ammonia at high hydrogen partial pressure is less of a poison to acid catalysts than organic nitrogen and would be tolerated in the second hydrocracking reactor. In one version of the process, separate hydrogen circulation systems are used for the two reactors, with an acid wash to remove ammonia and a carbonate wash to remove H<sub>2</sub>S from the hydrogen cycle.

Hydrocracking has become an integral part of refinery operations, with a U.S. capacity of about 900,000 bbl/d, but has lately encountered competition from hydrogenation (see section on metallic and multimetallic catalysis) and subsequent catalytic cracking, and capacity has remained fairly constant during the last five years.

V HYDROGENATION CATALYSIS AND HYDROGEN PRODUCTION

One of the oldest of catalytic reactions is the saturation of fats over nickel catalysts. In general, metallic catalysts have found their most widespread use in the activation of the hydrogen molecule.

a) Desulfurization and Denitrification

The greatest new industrial uses during the last 30 years have again occurred in the petroleum industry. With increasing supply of high-sulfur crude oils and the need to remove sulfur and nitrogen compounds for pollution abatement as well as to produce streams that can be subsequently treated over sulfur or nitrogen sensitive catalysts (e.g., in catalytic reforming, methanation, or hydrocracking), large hydrogenation units have been built, mostly to convert organic sulfur and nitrogen compounds to  $H_2S$  and  $NH_3$ , respectively, which in turn can then be removed by washes or adsorption. The most common catalysts used are cobalt-molybdena on alumina, molybdenum sulfide on alumina, and tungsten and/or nickel sulfide on supports. For the desulfurization of distillates, the operation is carried out at 500-700 psig (33-47 at) Pressure and temperatures of 600-800<sup>o</sup>F, (315-430<sup>o</sup>C) space velocities of 1-5 v/v/hr. The catalyst can be regenerated periodically by air burning, and catalyst life between regenerations is long--usually more than six months. This technology is derived from old German work of the 1930s, but found general use only in the 1950s.

More recently--in the late 1960s and early '70s--desulfurization of residual materials became important. This is more difficult, and catalyst poisoning is irreversible because of the deposition of heavy metals (V, Ni, Fe) from the oil on the catalyst. Conditions of this type of operation, pioneered largely by Gulf Oil and Esso, are more severe; pressures range up to 2000 psig (130 at) and space velocities are as low as 0.3 v/v/hr. It was found by workers that the pore

characteristics of the catalyst support are of great importance. Large pores are required to allow some of the very large carbon molecules containing hetero atoms to diffuse into the catalyst, while small pores are needed to provide the overall high surface area. (35) The technology has developed in two directions: 1) Catalysts with a very wide pore distribution have been used, ranging from  $10\text{\AA}$  to  $1000\text{\AA}$ ; 2) Catalyst beds have been graded with large pore catalysts first contacting the oil, and a decreasing pore-size catalyst treating partially converted feed. Hydrodesulfurization and hydrodenitrogenation catalysts are not selective to S and N compounds, and in all operations saturation of aromatics occurs as a side reaction, using up much more than the stoichiometric amounts of hydrogen required to convert sulfur or nitrogen compounds.

#### b) Selective Hydrogenation

Since 1975, considerable thought has been given to the hydrogenation of recycle stocks. These highly aromatic fractions from the catalytic cracking of heavy gas oils can be saturated, essentially in the type of operation described above, and are then suitable as catalytic cracking feeds. In many cases, this eliminates the need for hydrocracking.

Another application of hydrogenation is a selective one. In the steam cracking of ethane or naphtha to produce ethylene and propylene, a byproduct called pyrolysis gasoline is obtained which contains aromatics (benzene, toluene, xylenes) as well as olefins and diolefins. Before the aromatics can be extracted, it is necessary to saturate the olefins and diolefins without saturating the aromatics. Several commercial plants were built in the period between 1955 and 1965 using mostly nickel-sulfide catalysts for this treatment at relatively mild conditions. In a variant of the process, only the diolefins are saturated and the aromatic-olefinic product is blended as a high-octane component into gasoline.

Olefins produced from naphtha by steam cracking usually contain small but bothersome amounts of diolefins and acetylenes, such as butadiene, isoprene, and methylacetylene. These must be removed prior to polymerization of the olefins. This is usually done by selective hydrogenation over supported palladium catalysts under conditions that will not cause hydrogenation of mono-olefins.<sup>(36)</sup> Operating conditions are 35-100 °C and 3-30 atm. pressure. Nickel-cobalt-chromium catalysts have also been used for this purpose. In 1963, Farbenfabriken Bayer announced a liquid-phase selective hydrogenation process using a palladium catalyst which operates at very low temperatures. This has since been commercialized.

#### c) Hydrogen Production

Hydrogen for hydrogenation reactions comes mostly from two sources: reformer hydrogen, and the product from the steam-hydrocarbon (or steam-carbon) reaction. The steam-hydrocarbon reaction is called "steam reforming." It produces "synthesis gas," a mixture of hydrogen and carbon monoxide. The carbon monoxide is reacted over a water-gas shift catalyst with water to form more hydrogen and carbon dioxide, which can be scrubbed from the gas mixture leaving relatively pure hydrogen.

Hydrogen as a by-product from naphtha reforming has already been mentioned in the section on Dual Functional Catalysis. Production of hydrogen by steam reforming from methane, naphtha, heavy oil, and coal has achieved increasing importance in recent years. This is because of the increased demand for hydrogen, both for petroleum refining processes such as hydrotreating and hydrocracking, and for petrochemical use in the production of ammonia and methanol, among others. Steam reforming has recently been reviewed.<sup>(37)</sup>

While the reaction between carbonaceous material or hydrocarbons and steam over catalysts such as nickel on supports has long been known and used, a major breakthrough was achieved in 1962.<sup>(38)</sup>

Until then, the reaction of hydrocarbons and steam was limited to relatively low pressures. The reason for this is that, in addition to the reaction  $C + H_2O = CO + H_2$  and similar reactions for hydrocarbons, there is also a decomposition of hydrocarbons to produce carbon and hydrogen. The deposition of carbon on the catalyst rapidly deactivates the catalyst. At increasing pressures, this decomposition becomes faster at the temperatures involved than the reaction of steam and water. It was therefore necessary to accelerate the carbon-steam reaction so that it equaled or became faster than the hydrocarbon decomposition. This was achieved almost simultaneously by the M. W. Kellogg Company in the United States and the Imperial Chemical Industries (ICI) in Great Britain.<sup>(39)</sup> It was found that the carbon-steam reaction could be greatly accelerated by the presence of alkali or earth-alkali ions, and that catalysts containing sodium or potassium oxide in addition to the customary nickel<sup>(38)</sup> could perform at relatively high pressures up to 500 or 600 psig. (33 or 40 at) without this discovery, the new generation of ammonia plants (see following paragraphs) which operate at pressures of about 2000 psig (133 at) would not have been possible. By using a liquid feed such as naphtha or heavier hydrocarbons at pressures up to 500 pounds (33 at) which can be achieved by pumps, the remaining pressure difference of about 1500 psig (100 at) can be obtained by a single-stage compressor. The discovery of alkali promoted nickel catalysts for the steam-carbon reaction made possible a revolution in the ammonia industry and the creation of large-scale plants to produce ammonia at about one-half the cost of older generation plants. Alkali catalysts will also be important for the production of hydrogen and of methane from coal or char and water.

As already mentioned, if the production of hydrogen alone rather than synthesis gas is desired, it is necessary to react carbon monoxide with water to produce  $CO_2$  and hydrogen.<sup>(40)</sup> The exothermic water-gas shift process is used at 310-490 °C with an excess of water vapor; chromia-iron oxide catalysts are used with many improvements

in detailed catalyst composition having occurred during the past 20 years. Copper oxide-zinc oxide-alumina catalysts have also found application. Shift catalysts are available from several catalyst manufacturers.

#### d) Ammonia Synthesis

The synthesis of ammonia ( $N_2 + 3H_2 \rightarrow 2NH_3$ ) was discovered in the early part of the 20th century and has been widely described. The first plant was built in 1913 by BASF in Germany. While improvements have been made in the catalyst used, <sup>(41)</sup> these are of relatively minor importance and can be neglected in a history of industrial catalysis. Most catalysts are based on magnetite containing some alumina and CaO with alkali promoters. A major breakthrough, however, was achieved in the late 1950s when it became possible to build very large (1000 tons per day plus) ammonia plants of a simplified nature, and with greatly reduced investment and operating costs. The resultant reduction in the cost of ammonia increased the demand for ammonia as a fertilizer and has greatly contributed to avoiding famine in many parts of the world. This breakthrough is based on a combination of chemical and mechanical inventions. The chemical part of this invention, namely the production of hydrogen at relatively high pressures, has been detailed in a previous paragraph; the mechanical part of the invention consists of the introduction of single-train large units with one-stage centrifugal compressors rather than two or more stages of reciprocal compressors. Operation is being carried out at somewhat lower pressures than previously used (current operating pressures are in the order of 2000 psig (133 at)), even though equilibrium conditions are somewhat less favorable there than at higher pressure. However, this is greatly overcome by savings in operating and utility costs. Other mechanical improvements in ammonia synthesis include new reactor designs that permit greater efficiency. The first company to introduce the new design of ammonia plants was M. W. Kellogg.

Increased demand for ammonia as a result of these improvements is shown in Figure 13, which presents the size of individual plants as a function of time, and illustrates the rapid increase in capacity after the new generation of plants came into existence.

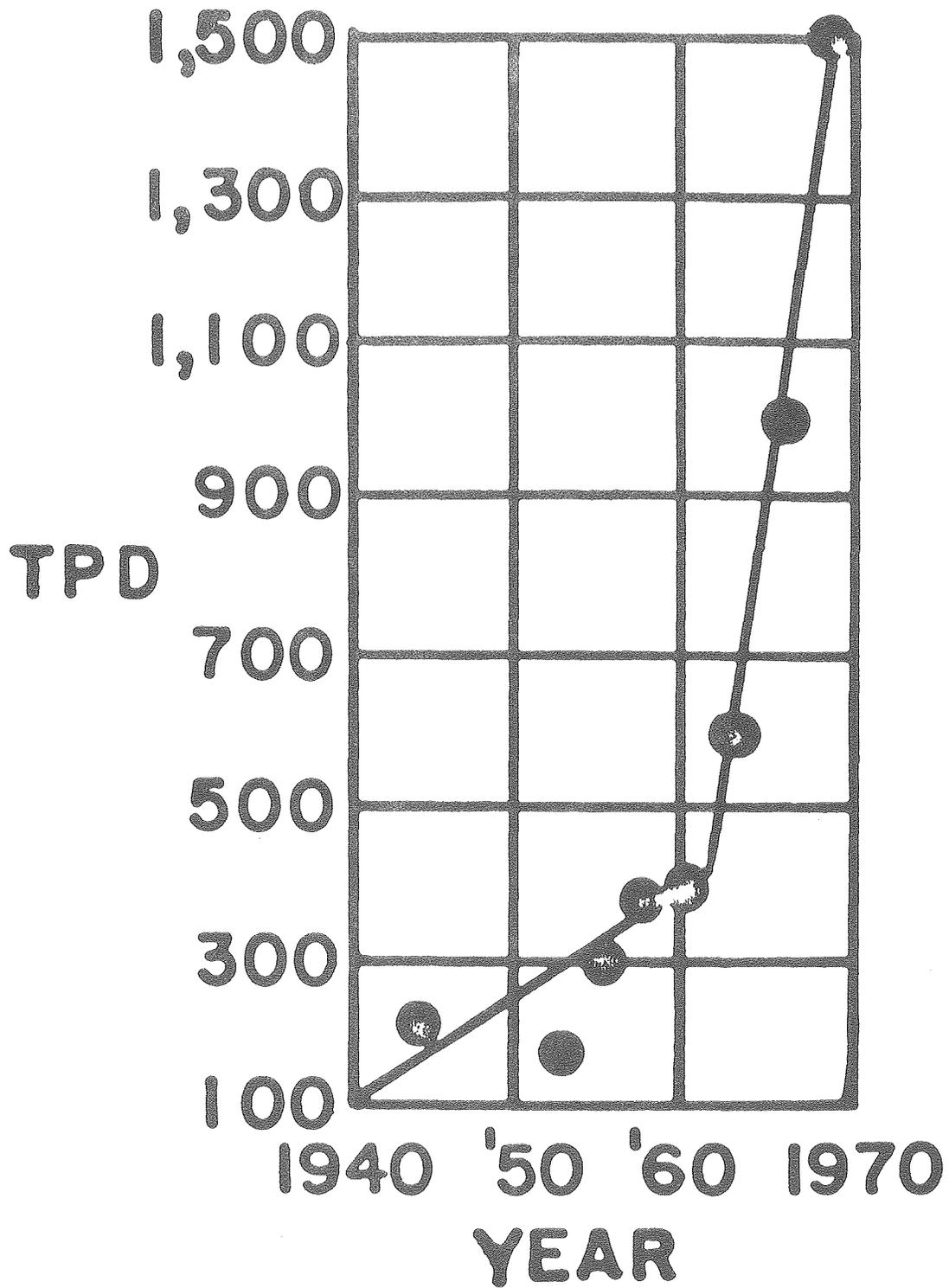
e) Methanol Synthesis ( $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$ )

The synthesis of ammonia and of methanol parallel each other in many ways. In fact, the unit design for the two processes is almost identical. Like ammonia, methanol synthesis dates back many years (it was commercialized in 1924). Mechanical improvements parallel those of ammonia synthesis. Chemical improvements were achieved around 1966 by Imperial Chemical Industries' discovery of a low-pressure methanol catalyst. This catalyst is comprised of zinc, copper, and alumina and permits operation at significantly less pressure (750 psig (50 at) vs. 2000 psig (133 at)) and lower temperature than the old historic zinc-alumina-chromia catalyst allowed, and has therefore contributed to a more economical production of methanol. ( 42 )

The advantages of a high-pressure production of synthesis gas as outlined above are applicable to the methanol synthesis as they are to the ammonia synthesis.

In addition to new catalyst developments, there have also been new reactor designs for methanol synthesis. The Lurgi reactor consists of a large number of relatively small-diameter catalyst-containing tubes. A bundle of these tubes is surrounded by a jacket filled with pressurized water. Control of the steam pressure in the jacket controls the temperature of the water, and provides an excellent heat-exchange medium for the exothermic methanol synthesis reaction.

These developments in ammonia and methanol syntheses are a clear demonstration of the fact that even technologies considered mature can undergo revolutionary developments that will change the demand-and-supply picture because of greatly reduced product prices.



XBL 793-9018

Fig. 13. Capacity of Individual Ammonia Units Built

## VI CATALATIC HYDROCARBON DEHYDROGENATION

Commercial dehydrogenation processes relate essentially to two types of operation involving different catalysts: 1) butane dehydrogenation to butenes and/or butadiene, 2) ethylbenzene dehydrogenation to styrene monomer.

Butane dehydrogenation was pioneered by Eugene J. Houdry and Houdry Process Corporation during World War II and has been reviewed in detail. ( 43 ) It is carried out to yield either butenes or butadiene, or both. Chromia-alumina is the preferred catalyst for this reaction. The catalyst is easily deactivated by steam, the presence of which during reaction must be avoided. Improvements made since installation of the first commercial plants in the mid-1940s are mostly of a mechanical nature and relate to operational time and conditions, and to catalyst regeneration time. Since the reaction is highly endothermic, heat generation for maintaining reaction temperature is dependent on burning coke deposits on the catalyst. A fine balance is required between coke lay-down and regeneration and operating time.

Oxidative dehydrogenation of butanes or butenes to butadiene is practiced over bismuth molybdate catalysts at 400-500°C. The exothermicity of oxidation supplies most of the heat requirements of the endothermic dehydrogenation. The impetus for commercial production of styrene in the United States lay in the critical need for a substitute for natural rubber during World War II. As a result of an industry-wide cooperative effort, an annual production capacity of over 400 (180) million pounds (Kg) was installed in only two years. This effort has been surveyed by Boundy and Boyer. ( 44 ) The best catalysts, still in use after more than 30 years, are comprised of alkali-promoted iron oxide and the reaction is carried out in the presence of steam to reduce hydrocarbon partial pressure. The best catalysts are unsupported. The major by-products from the dehydrogenation are benzene and toluene. A discussion of the effect of promoters on iron oxide can be found in E. H. Lee's review. (45 )

VII CATALYTIC DEALKYLATION

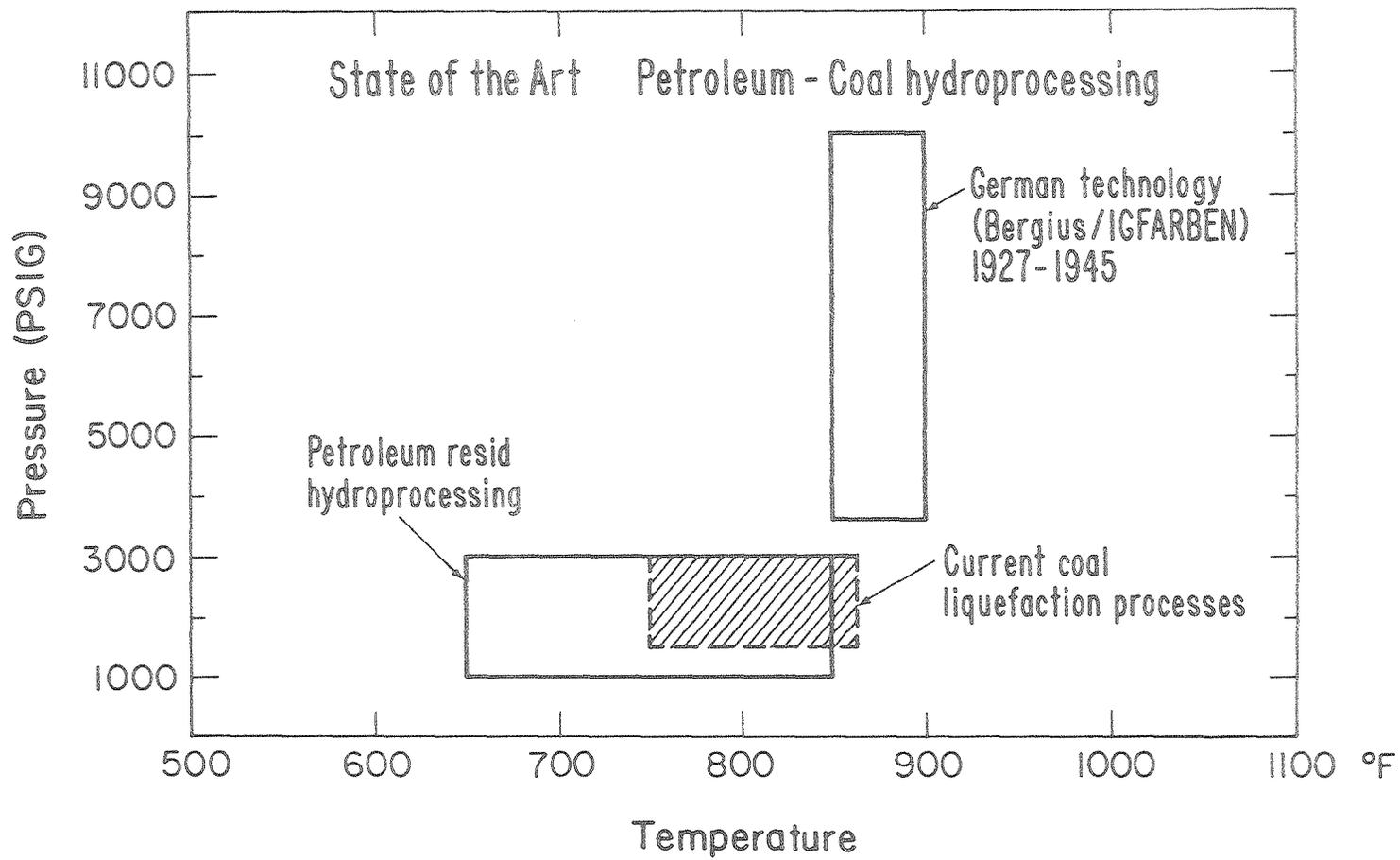
Hydro dealkylation is a process used for the production of benzene from toluene. Thermal as well as catalytic processes have been developed. Demethylation must be selective and hydrogenation of the aromatic ring must be avoided. High purity, low sodium chromia-alumina catalysts are used at 550-650°C and 35-80 at pressure ( 12 ). Because of the exothermicity of the reaction, close temperature control is required.

VIII CATALYTIC COAL LIQUEFACTION AND GASIFICATIONa) Liquefaction

Production of liquid fuels from coal is based on two technologies discovered in Germany in the 1920s: the Bergius process for direct catalytic hydrogenation in a solvent, and the Fischer-Tropsch process involving the reaction of coal and steam to produce synthesis gas ( $\text{CO} + \text{H}_2$ ) and subsequent hydrocarbon synthesis from this gas. Both technologies have been repeatedly reviewed. (46; 47; 48)

Both processes found large-scale commercial application in Germany during World War II, and a Fischer-Tropsch plant was built in South Africa in the mid-1940s and has been operating since, with a second larger facility to start operating in 1981, and a third one announced in 1979. While there was much active research on both the direct (hydrogenation) and the indirect (Fischer-Tropsch) liquefaction routes in the United States and in England during the 1940s and early '50s, interest lapsed when large volumes of inexpensive petroleum was discovered in the Middle East. Not until the 1970s was research intensified again, especially after the Arab oil embargo of 1974. No new commercial facilities other than the South African SASOL plant have been built as yet, but several new processes are being developed.

The new direct-hydrogenation processes are directed toward operating at lower-pressure and lower-hydrogen consumption than the Bergius process, as shown in Figure 14. Two of the three major processes being developed employ catalysts. In the H-coal process, the coal is dissolved in a recycle solvent containing largely aromatic and hydroaromatic hydrocarbons, and the resulting solution and/or slurry is contacted with a cobalt-molybdena alumina catalyst in an ebullating bed reactor. Catalyst life is said to be about one pound (0.5Kg) per ton of coal charged, or per 3 bbl of product. The operation is carried out at pressures in the range of 2000-3000 psig (133-200 at) and at temperatures of 750-850 °F. (400-450°C). After separation of the ash, products are fractionated and the solvent is recycled. Depending upon the



XBL 794-1052

Figure 14

Figure courtesy R. H. Fischer  
 U. S. Department of Energy

severity of the operation, the process operates in either a "syn-crude" or "fuel oil" mode. Hydrogen consumption is higher in the "syn-crude" mode (5000 cft/bbl) than in the "fuel oil" mode (3500 cft/bbl).

The "Exxon Donor Solvent" process distinguishes from the H-coal process by carrying out the hydrogenation by means of a donor solvent rich in hydroaromatics. This solvent is then rehydrogenated in a separate loop, using a conventional cobalt-molybdena catalyst. In this case, the catalyst is not subjected to potential poisons in the dissolved coal and slurried ash, and its life is therefore appreciably longer. The U. S. Department of Energy, jointly with industry, is currently sponsoring the erection and operation of large pilot plants for both processes.

The third major process (SRC) does not employ a catalytic reactor but it appears that the ash in coal possesses catalytic properties, which enhance thermal hydrogenation.

Indirect liquefaction also has been dormant until the mid-1970's, except for the SASOL plant. The major innovation at SASOL had been a fluid-bed operation of the synthesis reaction that permitted better temperature control and better yields of gasoline. H. Köelbel developed a liquid phase synthesis in a large pilot plant in Germany in 1948-1950.<sup>(49;50)</sup> Conventional iron-type Fischer-Tropsch catalysts are suspended in a heavy oil. High-per-pass conversions (95%+) are obtained and it is possible to operate with relatively low hydrogen/CO ratios such as 0.6/1. Internal shift supplies the additional hydrogen required. The low H<sub>2</sub>/CO ratio could be of increasing importance as new and less expensive gasifiers supplying low H<sub>2</sub>/CO-ratio gas become commercial.

A new development announced in 1976 is the Mobil methanol-to-gasoline process ( 21 ) mentioned in the section on zeolites. This process, for which a large pilot plant is currently under construction, will provide a new route from coal to high-octane gasoline, and appears to be competitive with other coal liquefaction routes.

### b) Gasification

In coal gasification there are two worthwhile developments. One involves the reaction of coal with steam in the presence of alkali carbonate. In the early and mid-1960's, the M. W. Kellogg Company did pilot plant work on a process in which coal dissolved in molten carbonate was reacted with steam to produce synthesis gas at high temperature and pressure.<sup>(51)</sup> Sulfur compounds in the coal react with alkali carbonate to form hydrosulfides which can then be reconverted to carbonate under high CO<sub>2</sub> particle pressure. In 1977, Exxon announced work on a process to produce methane directly from coal and water at relatively low temperatures by impregnating the coal with 7-10 percent of alkali carbonate. Complete recovery of the alkali carbonate has not yet been demonstrated.

Many coal gasification plants are in operation and many new designs are being developed. None of these employs added catalysts and the catalytic role of coal ash in gasification, if any, is not well defined.

### c) Methanation

Several methanation processes have been announced. The major catalytic step is the methanation of synthesis gas which takes place over a nickel catalyst. An interesting case is the use of a Raney nickel catalyst with which the reactor walls have been coated.<sup>(52)</sup> This is a novel technique and provides an alternative to supported nickel catalysts for the  $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4$  reaction.

## IX HETEROGENEOUS OXIDATION, AMMOXIDATION, CHLORINATION, AND OXYCHLORINATION CATALYSIS

---

### a) Oxidation

Oxidation of naphthalene  $\left( \text{C}_{10}\text{H}_8 \rightarrow \text{C}_8\text{H}_4\text{O}_2 \right)$  over molybdena or vanadia catalysts is an old art used for many years for the production of phthalic anhydride. In 1946, Oronite Company (now Chevron) initiated the production of phthalic anhydride from o-xylene over vanadium oxide catalysts. The feed can be impure because other C<sub>8</sub> aromatics and paraffins are oxidized to CO<sub>2</sub>. Considerable progress was achieved

when the first fluid-bed oxidation plants for naphthalene or o-xylene charges were built in 1952-1953 by Imperial Chemical Industries and American Cyanamid Company. Since then, the Badger-Sherwin Williams fluid-bed process has found application in several large plants. The better temperature control of the fluid bed has permitted better selectivities. Similar processes are used for oxidation of benzene to maleic anhydride, and of toluene to benzoic acid.

The conversion of light hydrocarbons into products containing oxygen or other heteroatoms is of great importance to the chemical industry. Ethylene oxide and ethylene glycol, propylene oxide, acrolein, acrylic acid, and acrylonitrile are all large-volume chemicals that are produced today from ethylene or propylene by catalytic oxidation or ammoxidation, resp.

Ethylene oxide<sup>(53)</sup> is a very large-scale commercial product. Early attempts to oxidize ethylene directly to the oxide failed. In 1931, Lefort first reported success using silver as a catalyst. Union Carbide first commercialized a direct oxidation process in 1937; and Scientific Design Company and Shell Oil Company have licensed many installations since then. Silver is still the major active catalyst ingredient. Promoters are used with the silver, such as oxides of alkali and alkaline earths. Organic halides minimize the formation of CO<sub>2</sub>. Ethylene oxidation processes are operated under recycle conditions in fixed-bed equipment at 250-325 °C and 10-50 atm. pressure. Conversion to ethylene oxide is about 70 percent, with much of the rest being lost to CO<sub>2</sub>.

A new catalytic process for production of propylene oxide from propylene was commercialized by Oxirane Company in 1969.<sup>(54; 69)</sup> Since it involves homogeneous catalysis, it is described in the section on Homogeneous Catalysis, as are other oxidation processes.

Hearne and Adams<sup>(55)</sup> described in 1948 the production of acrolein from propylene and oxygen  $(C_3H_6 + O_2 \rightarrow CH_2=CH-CHO + H_2O)$  over cuprous-oxide catalysts. Yields were about 50 percent. Further improvements by Shell involved a copper-oxide/silicon-carbide catalyst promoted by iodine.

A most important discovery was patented in 1959 by Idol and in 1962 by Callahan, <sup>(56; 57)</sup> who reported yields of acrolein much higher than those obtained in the old cuprous oxide system. The improvement was due to the selective action of a new type of catalyst--bismuth molybdate. Based on this discovery, Standard Oil Company of Ohio (SOHIO) commercialized vapor-phase propylene oxidation and ammoxidation processes.

#### b) Ammoxidation

Propylene, ammonia, and air are reacted in a fluid bed to give acrylonitrile and water ( $C_3H_6 + NH_3 + 1\frac{1}{2}O_2 \rightarrow CH_2=CH-CN + 3H_2O$ ) Operation is at 400-500°C and 3-30 psig (0.2-2at) pressure. A once-through operation without recycle is feasible and the process has found worldwide application. Even more selective catalysts of the novel uranium antimonate system were disclosed in 1965, and in 1970 SOHIO introduced "multicomponent" catalysts containing several elements of the group consisting of nickel, cobalt, iron, bismuth, molybdenum, potassium, manganese, and silicon. Production of acrylonitrile by this type of catalysis was 2.5 million tons/yr in 1977. <sup>(17)</sup>

An alternative propylene oxidation route using tin plus antimony oxides as catalysts was also developed by SOHIO. <sup>(54; 58)</sup>

A process which is somewhat related to ammoxidation involves the synthesis of methylpyridines from ammonia and acetaldehyde. It is carried out over silica-alumina catalysts, modified by thorium, zinc, or cadmium at 750-950 °F. (400-510°C) It gives yields of 40-60 percent.

#### c) Hydrohalogenation and Oxychlorination

Catalysts comprising inorganic metal chlorides have found application in hydrohalogenation reactions. Thus, bismuth and

antimony trichloride are used to add HCl to ethylene or propylene and mercuric chloride on carbon is a common catalyst for reacting acetylene with HCl to produce vinyl chloride.

Oxidation of HCl to chlorine over cupric chloride was first described by Deacon about 100 years ago. Attempts to operate a process on this reaction failed because of major corrosion problems. In 1969, M. W. Kellogg Company announced a successful process (which is discussed in the section on Homogeneous Catalysis).

In 1964, Goodrich, Dow, and Monsanto commercialized oxy-chlorination processes. (58; 59) Most of these are fixed- or fluid-bed operations over copper chloride catalysts, reacting ethylene and HCl and oxygen to dichloroethane and water. The copper salts are molten and sorbed in the alumina support at operating conditions; HCl produced in the direct chlorination of ethylene can thus be converted into the desired vinylchloride monomer. This development followed an earlier operation of the Raschig-Hooker process, in which benzene is chlorinated to chlorobenzene by the reaction of benzene with HCl and oxygen over copper chloride on an inert support.

Chlorides of rare earths and alkali metals often serve as promoters for  $\text{CuCl}_2$  in oxychlorination. Workers at the M. W. Kellogg Company (60) have described a homogeneous version of the oxychlorination process, using an aqueous solution of copper salts. This has the advantage of easy heat removal by water evaporation.

#### d) Hydrogen cyanide

The formation of hydrogen cyanide from ammonia, methane, and oxygen over rhodium or iridium-promoted platinum was disclosed by Andrussow some time ago ( $\text{CH}_4 + \text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{HCN} + 3\text{H}_2\text{O}$ ) and was commercialized using promoted platinum gauze, similar to the process used to make nitric acid from ammonia. An improvement of the Andrussow process was commercialized in the 1950s by Degussa. In this process, small diameter refractory tubes are coated with the catalyst and the reaction proceeds on the reactor walls. In this case no oxygen is required and the process produces hydrogen according to  $\text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2\text{O}$ .

## X OLEFIN DISPROPORTIONATION CATALYSIS

A new catalytic reaction was disclosed by Banks and Bailey in 1964.<sup>(61;62)</sup> Called "olefin disproportionation," it converted linear olefins into homologs of shorter and longer chains in a highly specific and efficient manner. The total moles of product olefins heavier than the feed equaled the total moles of lighter olefins. Propylene for example could be converted to ethylene and butenes ( $2C_3H_6 \rightarrow C_2H_4 + C_4H_8$ ). While the original discovery involved the use of molybdenum or tungsten hexacarbonyl catalysts supported on alumina, many other catalysts--both heterogeneous and homogeneous--have since been reported for this reaction.<sup>(63)</sup> Table 4 shows some of the heterogeneous support and promoter combinations used. Typical homogeneous catalysts described in the literature are those obtained by interaction of tungsten hexachloride, ethanol, and ethylaluminum dichloride, or by reaction of nitrosyl complexes of halides.

The first commercial application of the new process chemistry occurred in 1966. Shawinigan Chemicals Company in Canada installed a Phillips Petroleum Company "Triolefin" process unit to convert propylene into polymerization-grade ethylene and high purity butenes. Other installations have been installed since then.

## XI INDUSTRIAL HOMOGENEOUS CATALYSIS

Applications of homogeneous catalysis have greatly increased in recent years. Where sulfuric acid catalysed alkylation and the cobalt carbonyl catalysed Oxo reaction ( $CH_3CH=CH_2 + CO + H_2 \rightarrow C_3H_7CHO$ ) were almost alone in this field 25 years ago, there are now over 20 industrial processes. Most employ soluble metal compounds as catalysts. Monomers and polymers are the major products. G. W. Parshall has recently published a review of homogeneous catalytic processes,<sup>(64)</sup> and Table 5 summarizes some major applications.

Table 4<sup>(63)</sup>Olefin Disporportionation Catalyst Supports  
and Promoters

	Supports	Promoters
OXIDES	Al Si Fe	Mo W Re
	Ni Zr Sn	Nb Rh Sn
	W Th SiAl	Te La Ta
	AlTi AlTh MgSi	Os Ir
	MgTi	
PHOSPHATES	Al Ti Ca	
	Zr Mg	
HEXACARBONYLS		Mo W Re
SULFIDES		Mo W

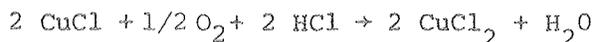
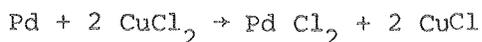
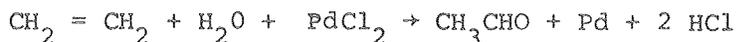
Table 5<sup>(64)</sup>Major Applications of Homogeneous Catalysis  
in the U.S. Chemical Industry

	Approximate 1975 capacity or pro- duction (thousands of metric tons)
<b>Carbonylations</b>	
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2 \longrightarrow \text{C}_3\text{H}_7\text{CHO}$ (includes other oxo products)	650 p
$\text{RCH}=\text{CH}_2 + \text{CO} + 2\text{H}_2 \longrightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{OH}$	170 c
$\text{CH}_3\text{OH} + \text{CO} \longrightarrow \text{CH}_3\text{COOH}$	190 c
<b>Monoolefin Reactions</b>	
$\text{CH}_2=\text{CH}_2 + \text{O}_2 \longrightarrow \text{CH}_3\text{CHO}$	410 p
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{ROOH} \longrightarrow \text{CH}_3\text{CH} \begin{array}{c} \diagup \quad \diagdown \\ \quad \quad \text{O} \end{array} \text{CH}_2 + \text{ROH}$	250 c
$\text{CH}_2=\text{CH}_2 \longrightarrow$ Polyethylene (excludes oxide supported catalysts)	150 c
$\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}=\text{CH}_2 + \text{diene} \longrightarrow$ EPDM rubber	85 p
<b>Diene Reactions</b>	
$3\text{CH}_2=\text{CHCH}=\text{CH}_2 \longrightarrow$ cyclododecatriene	10 p
$\text{C}_4\text{H}_6 + \text{CH}_2=\text{CH}_2 \longrightarrow$ 1,4-hexadiene	2 p
$\text{C}_4\text{H}_6 + 2\text{HCN} \longrightarrow \text{NC}(\text{CH}_2)_4\text{CN}$	70 c
$\text{C}_4\text{H}_6 \longrightarrow$ <i>cis</i> -1,4-polybutadiene	290 p
<b>Oxidations</b>	
$\text{c-C}_6\text{H}_{12} \xrightarrow{\text{O}_2} \text{c-C}_6\text{H}_{11}\text{OH} + \text{c-C}_6\text{H}_{10}=\text{O} \xrightarrow[\text{HNO}_3]{\text{O}_2 \text{ or}} \text{adipic acid}$	610 p
$\text{c-C}_{12}\text{H}_{24} \xrightarrow{\text{O}_2} \text{c-C}_{12}\text{H}_{23}\text{OH} + \text{c-C}_{12}\text{H}_{22}=\text{O} \xrightarrow[\text{HNO}_3]{\text{HNO}_3} \text{dodecanedioic acid}$	10 c
$\text{CH}_3 \text{  } \text{CH}_3 \xrightarrow{\text{O}_2} \text{terephthalic acid and esters}$	2 100 p
$\text{n-C}_4\text{H}_{10} \xrightarrow{\text{O}_2} \text{CH}_3\text{COOH}$	470 p
$\text{CH}_3\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_3\text{COOH}$	335 p
<b>Other Reactions</b>	
$\text{CH}_2=\text{CHCHClCH}_2\text{Cl} \rightleftharpoons \text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl}$	270 p
$\text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl} + 2\text{NaCN} \longrightarrow \text{NCCH}_2\text{CH}=\text{CHCH}_2\text{CN}$	125 c
$\text{ROOC} \text{  } \text{COOR} + \text{HOCH}_2\text{CH}_2\text{OH} \longrightarrow \text{polyester}$	1 900 p

Olefin polymerization is probably the largest scale application of organometallic catalysed processes. Many of the catalysts used in the process technology initiated by Ziegler and Natta<sup>(72)</sup> are not soluble and therefore are discussed separately. However, a significant amount of linear polyethylene is produced with soluble titanium catalysts. Ethylene-propylene-diene elastomers and stereoregular polybutadiene are produced with analogous catalyst mixtures based on other transition metal compounds.

In 1938-1946 Roelen in Germany developed the Oxo process, still one of the largest applications of homogeneous catalysis. It involves hydroformylation, the reaction of an olefin with carbon monoxide and hydrogen to produce aldehydes (e.g., butyraldehyde from propylene or propionaldehyde from ethylene) and fatty alcohols from higher olefines. Cobalt carbonyls were the usual catalysts.<sup>(65)</sup> They were generated in-situ from cobalt salts and synthesis gas ( $\text{CO} + \text{H}_2$ ) in the presence of a base. They are used at 200-300 atm. pressure and 100-150 °C. A major improvement in catalyst technology was made when Union Carbide commercialized in 1976 the production of butyraldehyde from xylene employing homogeneous rhodium catalysts containing a phosphine ligand. The new catalysts operate at much lower pressure, e.g., 10-25 atm. and at low temperature ( $\sim 100$  °C).

In 1960, a major advance in metallorganic catalysis occurred when Wacker Chemie, a subsidiary of Höchst, introduced a simple high-yield process for producing acetaldehyde from ethylene.<sup>(66)</sup> This process practiced in the United States by companies such as Celanese and Texas Eastman has largely displaced syntheses based on ethanol or acetylene. The oxidation of ethylene is carried out either as a two-stage process using air, or as a one-stage process using oxygen. The oxidizing catalyst is an aqueous solution of cupric chloride and palladium chloride and proceeds in three steps:



Ethylene is oxidized by water and palladium chloride. The resulting palladium metal is reconverted to palladium chloride by cupric chloride. The cuprous chloride is reoxidized by air or oxygen. Farbenfabriken Bayer has introduced a heterogeneous version of this catalyst. The same type of homogeneous catalysis is also used to produce vinyl acetate from ethylene and acetic acid.

Acetic acid is produced by oxidation of acetaldehyde with soluble metal catalysts. The largest type of process, though, is based on the carbonylation of methanol.<sup>(67)</sup> Badische Anilin and Sodafabrik (BASF) pioneered a process that has been used in the U.S. by Borden Chemical Company since 1968. It uses a cobalt carbonyl catalyst promoted by iodine. More recently, Monsanto commercialized in 1977 a process employing rhodium complexes and methyl iodide as cocatalysts.<sup>(68)</sup> The Monsanto process uses milder process conditions and exhibits very high selectivity to acetic acid, but must, to be economical, recover almost all of the rhodium.

According to Parshall, one of the largest applications of homogeneous catalysis is the production of terephthalate esters. P-xylene is oxidized by air using soluble cobalt and manganese salts as catalysts. Amoco Chemicals Company is a major user of this process.

An interesting new process was discovered and commercialized in 1969 by Oxirane Corporation.<sup>(69)</sup> Propylene is oxidized to propylene oxide by t-butyl hydroperoxide, catalysed by soluble molybdenum compounds such as molybdenum carbonyl. The t-butylhydroperoxide is obtained by air oxidation of isobutane. T-butyl alcohol is a co-product with propylene oxide. This process is finding application

in various parts of the world and is replacing older methods of propylene oxide manufacture.

Also, in 1969 the M.W. Kellogg Company announced a different type of homogeneously catalysed process, a new version of the old Deacon process to convert HCl to chlorine. The "Kelchlor" process<sup>(70)</sup> has been commercialized on a large scale by E.I. duPont de Nemours & Company. It uses oxides of nitrogen as the catalyst in combination with a powerful dehydrating agent,  $H_2SO_4$ . The latter permits the reaction to proceed beyond equilibrium constraints, since it effectively removes water of reaction from the reaction product. The process is of particular use in conjunction with chlorination reactions, since it permits the by-product HCl to be reconverted to chlorine.

A very large-scale application of dissolved catalysts is the production of dichloroethane from ethylene and chlorine, employing  $FeCl_3$ ,  $CuCl_2$ , or  $SbCl_3$ . The dichloroethane is then thermally dehydrochlorinated to vinyl chloride.

## XII CATALYTIC POLYMERIZATION

Polymerization catalysis is an important and relatively old field. Before and during the second World War, efforts were largely concentrated on dimerizing and trimerizing ethylene and propylene to high-octane gasoline.<sup>(71)</sup> Work was also done to obtain higher molecular weight products in the lubricating oil boiling range. With the need for synthetic rubber spiraling during World War II, technology was developed for butadiene polymers and butadiene-styrene as well as isobutylene-isoprene copolymers. Numerous improvements have been made in the polymerization of these and other monomers, such as vinyl chloride, which cannot be enumerated here.

After World War II the polymer industry began to develop rapidly, and polyethylene--and to a somewhat lesser extent polypropylene--became articles of large-scale commerce. The high-pressure polyethylene

process commercialized by Imperial Chemical Industries in England, BASF in Germany, and others involved a thermal free radical process at pressures of 1000 atm. and more, and it dominated the field until major discoveries were made by Karl Ziegler in Germany and G. Natta in Italy. These men later shared a Nobel Prize in 1964 for their contributions.

Ziegler disclosed in 1955 a catalyst system<sup>(72)</sup> that would polymerize ethylene to polyethylene at low pressures, e.g., 10 atm. (The "low-pressure" polyethylene is more linear, has a higher melting point, and is more rigid than "high-pressure" polyethylene.) Catalysts spanning the homogeneous-heterogeneous interface were used (see also the section on Homogeneous Catalysis). One such catalyst is prepared from aluminum alkyl, e.g., Al Et<sub>3</sub> and titanium tetrachloride, using an excess of the alkyl.<sup>(73)</sup> The preparation is carried out in a dry hydrocarbon solvent, usually hexane. The precipitate plus the aluminum alkyl still in solution is "the catalyst." The reaction is carried out at 50-75 °C and about 10 atm. pressure, and the polymer forms as a white powder suspended in the solvent. Many catalyst modifications have been developed by various manufacturers. In the Amoco Chemical Company process,<sup>(74)</sup> which operates at 240-300 °C and 35-100 atm. pressure, the catalyst is molybdic acid on alumina, plus reducing agents such as aluminum alkyl, lithium borohydride, or metallic sodium as co-catalysts. The Phillips Petroleum Company catalyst<sup>(75)</sup> comprises chromium trioxide on silica or alumina in cyclohexane as the solvent. Promoters are used, as shown in Table 6.<sup>(76)</sup>

G. Natta in 1969 described the polymerization of propylene and higher  $\alpha$ -olefins to highly ordered, crystalline polymers. "Isotactic" polypropylene has the carbon atoms in each succeeding propylene unit ordered in the same identical way. C. L. Thomas<sup>(73)</sup> refers to a statement by Natta that the term "isotactic" was suggested by Mrs. Natta because the structure reminded her of the ordered lines and columns of marching soldiers.

Table 6<sup>(72)</sup>

## Some Oxide Promoters for Supported Chromia Catalysts

SUPPORT →	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	ThO <sub>2</sub>
PROMOTER ↓	CuO			
	ZnO	ZnO		
	SrO	SrO		
	WO <sub>3</sub>			
	Mn <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>		
	Co <sub>2</sub> O <sub>3</sub>			
	Fe <sub>2</sub> O <sub>3</sub>			
		MgO		
		BaO	BaO	
		B <sub>2</sub> O <sub>3</sub>		

Natta requires a crystalline or microcrystalline catalyst for the production of stereospecific products. Crystalline  $\alpha$ -titanium trichloride plus aluminum alkyl constitutes such a catalyst system. Operating conditions of this type of catalyst for propylene polymerization are similar to Ziegler's, except for slightly higher temperatures.

The Ziegler and Natta discoveries have resulted in applications of great technological importance, and over one-half of all olefin polymers produced is based on this technology.

Urethane foams constitute an important item of plastics manufacture. They are obtained from isocyanates and alcohols, particularly diols in the presence of some water. The reaction is catalytic and most of the product is manufactured using a catalyst first introduced in 1959 by Houdry Process Corporation, called "Dabco" (triethylene diamine).<sup>(77)</sup> This is often promoted by organic stannous compounds. The commercial use of this catalyst combination appears to have been the first introduction of an organic compound as a catalyst. DABCO has such high activity that it permits a one-step process.

### XIII CATALYSIS FOR MOTOR VEHICLE EMISSION CONTROL<sup>(78)</sup>

It is a rare event when a whole new field of catalytic applications opens up. This happened when the State of California enacted laws on air quality and motor-vehicle emissions standards in 1959 and 1960. These laws were to go into effect when at least two devices had been developed that could meet these standards. While these laws stimulated a considerable amount of research, one should not omit mention of the fact that Eugene J. Houdry, the pioneer of so much industrial catalysis (see sections on Catalytic Cracking and Dehydrogenation), foresaw the need for emission control--at least in confined spaces--as early as 1949, and developed catalytic mufflers for indoor vehicles, marketed by Oxy-Catalyst, Inc. One of these early catalysts consisted of monolith-porcelain rods covered

with alumina upon which platinum was deposited. This anticipated later developments.

Following the California law enactment, three groups of catalyst and muffler manufacturers were certified by the California Motor Vehicle Control Board in 1964 and 1965. These were W. R. Grace—Norris Thermador, Universal Oil Products—Arvin, and American Cyanamid—Walker. However, engine modifications by the car manufacturers enabled them to meet specifications without the use of catalysts.

The U.S. Federal Clean Air Act of 1970 set requirements that could not be met by existing technology, and this spurred an intensive research effort. Although enforcement of the law was later delayed by one year, from 1975 to 1976, and the law was modified by setting interim standards, catalytic mufflers have been installed on all new cars in the U.S. since 1976. The only exception has been Honda cars which used an improved mechanical system.

Among the numerous organizations doing research and development in this area during this period was a combination of companies doing joint research in the "Interindustry Emission Control Program." The group consisted of Ford Motor Company, Mobil Oil Corporation, Volkswagen, Toyota, Fiat, and others.

The initial objective of emission control research was to reduce carbon monoxide and hydrocarbon emissions to specified levels, 90 percent or more below those previously emitted. The reduction of nitrogen oxide emissions was undertaken somewhat later. A totally new problem for catalytic reactor design was immediately recognized. While most industrial catalytic operations involve continuous and steady-state conditions, automobile operations are intermittent and transient, with wide fluctuations of flow rate and temperature that depend on driving conditions and cold or warm engine starts.

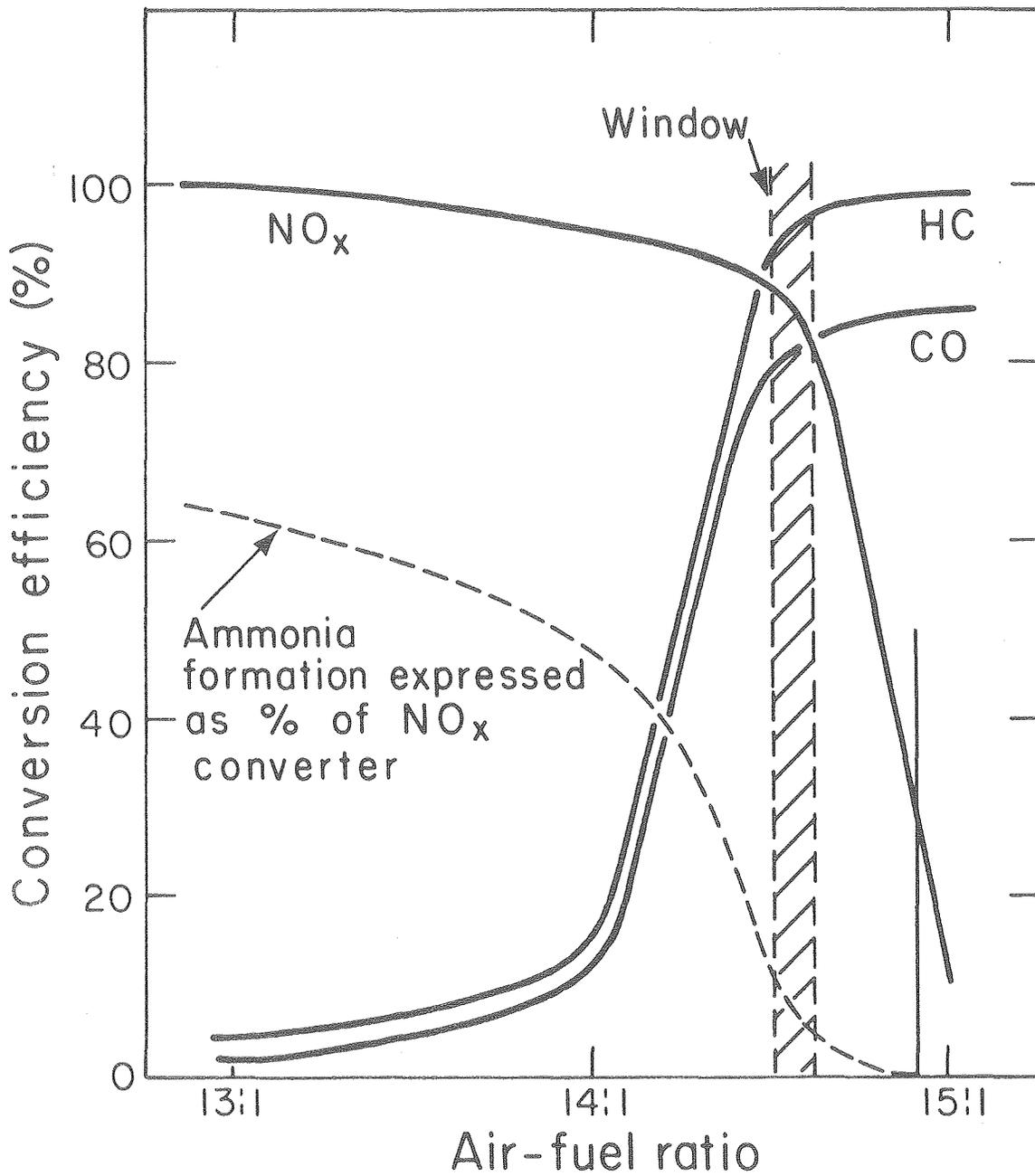
As shown in J. Wei's review of the field, <sup>(78)</sup> exhaust gas-flow rates can vary from 20 to more than 200 SCF/min, and

exhaust temperatures from 600 to 1800 °F (351-980°C) plus. Many materials such as base-metal oxides and alloys oxidize CO and hydrocarbons to CO<sub>2</sub> at quite high conversions. Requirements are, however, that more than 90 percent of CO and hydrocarbons be removed at space velocities of up to 200,000 V/V/hr within a temperature range of about 500-2000 °F. (260-1100°C) In addition, the oxidizing atmosphere contains 15 percent water and not much more than a stoichiometric amount of oxygen. The catalyst, further, must last for at least 25,000 vehicle miles.

Only precious metal catalysts have thus far been used commercially to meet the many difficult specifications. In most cases, the metal is dispersed as small crystallites on thermally stable, chemically inactive supports such as α-alumina. Three major support shapes comprise spheroids, wire mesh, and monolithic honeycombs. A "washcoat" of high-surface-area alumina is usually placed on the ceramic surface and acts as substrate for the precious metal

A major requirement for the use of platinum-type emission catalysts has been the elimination of potential poisons from the gasoline, most prominently the lead compounds. All cars having catalytic mufflers must use lead-free gasoline. This has resulted in the inability to boost octane number by addition of tetraethyl lead to gasoline, and in the need to produce relatively high-octane (91-93 Research) gasoline by catalytic reforming or cracking; it has increased the amount of crude oil processed, since yield of gasoline decreases with increasing octane requirement.

The amount of precious metal used in emission control devices is about 0.05 troy oz/car. Reactor design is complex, since high pressure drop must be avoided at very high space velocities. Manufacturers of commercial emission control catalysts in the U.S. include Engelhard, W. R. Grace & Company, Universal Oil Products Company, The Catalyst Company, and the Houdry Process Division of Air Products & Chemicals, Inc.



XBL 796-1707

Fig. 15. "Three-way" Redox Catalyst Conversion Characteristics.

Figure taken from reference 78.

In addition to CO and hydrocarbon emission standards, specifications for  $\text{NO}_x$  emissions have been set for 1977 and later cars in the United States. Three-way precious metal "Redox" catalysts can take advantage of a "window" at an air/fuel ratio of exactly 14.7:1, at which  $\text{NO}_x$  conversion is still high and CO and hydrocarbon conversion is very substantial (all conversions > 80%)(Fig.15.) However, the window is so narrow that maintenance of this air/fuel ratio is difficult. Proposals for a separate  $\text{NO}_x$  catalyst bed have thus far not been commercialised. For the total catalytic system, two converters or a converter containing a dual-bed catalyst will probably be necessary. The first bed will catalyse the reduction of nitrogen oxides to nitrogen, while the second oxidizes hydrocarbons and CO to  $\text{CO}_2$  and water. Three-way converters will be required to meet the 1981 standards.

Development of catalysts for automotive emission control has been and is a great challenge because of the extreme mechanical and operating condition variations encountered. The use of catalysts in cars in 1978 is shown in Table 7.<sup>(17)</sup>

#### XIV FUEL CELL CATALYSIS

Catalysts are used at both the anode and cathode of a fuel cell. Hydrogen has been the most common fuel. It is oxidized at the anode and the oxidant is reduced at the cathode. While much research has been undertaken on fuel-cell catalysis, industrial applications are thus far very limited. Fuel cells were used in the Gemini and Apollo space crafts using noble metal on carbon catalysts. A large electric utility demonstration is planned by Consolidated Edison in New York for 1979. This unit will generate about 5 megavolts. (79)

#### XV THE PROFESSION OF CATALYTIC CHEMISTS AND ENGINEERS

While catalysis as it has been discussed is an old art and quite old a science, until the last quarter of this century it has functioned essentially as a part of various branches of

Table 7<sup>(17)</sup>Use of Catalysts in Cars  
in 1978

Material	Estimated use*	Estimated value* (million dollars)
Alumina pellets	37.6 million lbs.	\$71.0
Cordierite monolith	8.9 million lbs.	34.0
Alumina wash coat	1.6 million lbs.	1.4
Platinum	395,000 troy oz.	93.6
Palladium	130,000 troy oz.	9.2
Total		\$209.2

\*For installation on cars manufactured in the U.S. last year.  
Actual use would be at least 10% higher because of  
converters for Canadian cars and spares.

of chemistry (physical, organic, inorganic), physics, and engineering (reactor engineering, modeling).

A first international meeting, primarily devoted to catalytic research, was held by the Faraday Society in 1949. The annual Gordon Research Conferences on Catalysis started in 1943 as the Gibson Island Conferences, and moved to Colby Junior College in New Hampshire in 1946 as part of the Gordon Research Conference. A whole generation of catalytic scientists has attended these prestigious and pleasant meetings restricted to about 100 persons.

In 1949, a group of seven scientists gathered in Philadelphia to discuss the possibility of holding regular local meetings in the field of catalysis. They were A. Farkas, F. G. Ciapetta, R. Hansford, H. Heinemann, R. Kennedy, K. A. Krieger, and A. G. Oblad. These men started the Catalysis Club of Philadelphia, which from that time on held monthly meetings. All of the founders served as chairmen of the Club in its early years. First-year meetings were held at the University of Pennsylvania, and attendance at the meetings rapidly increased from about 15 to 80-100 persons. Men prominent in the field like D. A. Dowden, P. H. Emmett, and Otto Beek, were among the first speakers. Beginning in 1951 an annual all-day symposium was held--a custom that still prevails. The first symposia were on Saturdays at Swarthmore College, then at the DuPont Country Club in Wilmington, and later in Princeton, New Jersey and in Chester, Pennsylvania. Membership of the Philadelphia Club rapidly increased to above 200 and has remained at that level. A Chicago Catalysis Club was founded a few years later, followed by the New York Club--whose founders were charter members of the Philadelphia Club. Within the next 20 years, catalysis clubs were formed in California, New England (Boston), Pittsburgh, Houston (Southwest Catalysis Club), Michigan, and also in Canada. In 1979, the Tri-State Catalysis Society joined the group.

In 1954, Rudolf Brill and Heinz Heinemann suggested to the Philadelphia Club that an International Congress on Catalysis should be held, and the Club under its chairman, G. A. Mills enthusiastically sponsored the First International Congress of Catalysis in Philadelphia in 1956. P. H. Emmett, Eric Rideal, and Eugene Houdry were honorary chairmen, and Heinz Heinemann was executive secretary of the event with responsibility for the overall organization. Numerous committee chairmen worked hard to make the Congress a success and they, as well as the sponsors who contributed \$43,000 to the Congress, are listed in Volume 9 of *ADVANCES IN CATALYSIS* that contains the proceedings of the meeting. The Congress was attended by over 600 persons, many of whom came from abroad with the support of part of the funds raised for the event. During preparations for the meeting, the "International Congress on Catalysis" was incorporated in the U.S., and at the meeting it was decided to hold such Congresses once every four years in a country offering an invitation. Heinz Heinemann was elected president of the organization for the period 1956-1960 and through the second Congress held in Paris in 1960. He was succeeded as president by A. Farkas (1960-1964), F. G. Ciapetta (1964-1968), and V. Haensel (1968-1972). The Third Congress was held in Amsterdam in 1964, the fourth in Moscow in 1968, the fifth in Palm Beach, Florida in 1972, the sixth in London in 1976, and the seventh is scheduled for 1980 in Tokyo. All Congresses after the first five were attended by at least 1000 participants, and proceedings have been published for all of them. The Second Congress was cosponsored by IUPAC, and subsequent ones were joint enterprises. After the success of the Second Congress, a truly international organization was established with a board comprising two representatives from each member country. Local organizing committees did most of the work.

By 1965, the individual catalysis clubs in the United States felt the need for closer affiliation, and the Catalysis Society of North America was established, which comprised the membership of

all catalysis clubs that were renamed "Catalysis Society of California," etc. The organization of the Catalysis Society and of its first national meeting in Atlantic City in 1969 were financed with funds remaining from the First International Congress on Catalysis. National meetings of the Society have been held every two years in odd-numbered years in Atlantic City, New Jersey, Houston, San Francisco, Toronto, Pittsburgh, and Chicago. All have been attended by hundreds of participants and parallel scientific sessions have been required. The Society is administered by a Board of Directors elected by the member societies and the membership at-large. The Board in turn elects a president, or vice-president, secretary, and treasurer.

In 1967, the Catalysis Society of North America proposed the establishment of two prestigious awards to be given once every two years. A committee comprised of A. H. Weiss and Heinz Heinemann obtained sponsorship for the "Paul H. Emmett Award" in fundamental catalysis and the "Eugene J. Houdry Award" in applied catalysis-- the former to carry a \$2000 prize and the latter a \$2500 prize. The Emmet Award has been sponsored since its inception by the Davison Division of W. R. Grace & Company; the Houdry Award was originally sponsored by the Houdry Process Corporation, Sun Oil Company, Oxycat Corporation, and the Houdry family. More recently, Air Products and Chemicals Corporation has taken over a good part of the sponsorship. Award winners for the first ten years were:

<u>Emmett Award</u>	<u>Houdry Award</u>
R. Kokes	H. Bloch
J. H. Sinfelt	C. Plank
J. Lunsford	H. Heinemann
G. A. Somorjai	V. Haensel
G. Ertl	A. Farkas

Catalysis Clubs have also prospered in other countries. There are now such groups in Hungary, Japan, and Holland.

The Gordon Conferences found a European equivalent in the Roremont Conferences held in Holland for the past ten years.

ACKNOWLEDGEMENT

This work was supported by the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory under the auspices of the U. S. Department of Energy, Contact Number W-7405-Eng-48.

XVI REFERENCES

1. Mills, G. A. and Cusumano, J. A. Catalysis. In Kirk-Othmer: Encyclopedia of Chemical Technology (3rd Ed., Vol. 5). New York: John Wiley, 1979.
2. Gurwitsch, L. Kolloidz., 1912, 11(17).
3. Herbst, H. Erdöl und Teer, 1926, 2(265), 411.
4. Sachanen, A. N. Conversion of petroleum (2nd Ed.). New York: Reinhold, 1948.
5. Sittig, M. Pet. Refiner, 1952, 31(9), 263.
6. Ardern, D. B., Dart, J. C., and Lassiat, R. C. Adv. in Chem., 1951, 5(13).
7. Murphree, E. V. Adv. in Chem., 1951, 5(30).
8. Venuto, P. B. and Habib, E. T. Cat. Rev., 1978, 18(1).
9. Oblad, A. G. Oil Gas Journal, 1963, 61(13), 124.
10. Blazek, J. J., Grey, F. E., Jr., and Baker, R. W. Proceedings API Division Refining, 1962, 42(3), 277.
11. Emmett, P. H. Catalysis (Vols. 1-7). Reinhold Publishing Co., New York, 1954-60.
12. Thomas, C. L. Catalytic processes and proven catalysts. Academic Press, New York, 1970. pp. 87ff.

13. Gunness, R. C. Adv. in Chem., 1951, 5(109).
14. Rabo, J. A., Pickert, P. E., Stamires, D. N., and Boyle, J. E. Proceedings of 2nd International Congress on Catalysis (Edition Tech.), Paris, 1960. (P. 2055)
15. Eastwood, S. C., Plank, C. J., and Weisz, P. B. Proceedings of the 8th World Petroleum Congress, Edinburgh, 1971, Neil & Company, Ltd.
16. Plank, C. J., Rosinsky, E. J., and Hawthorne, W. P. I&EC Product Research and Development, 1964, 3(165).
17. Burke, D. P. Chem. Week, 1979, 124(13), 42.
18. Oblad, A. G. Oil Gas Journal, 1972, 70(13), 84.
19. Weisz, P. B., Frilette, V. J., Maatman, R. W., and Mower, E. B. J. Cat., 1962, 1(307).  
Weisz, P. B. and Frilette, V. J. Journal Phys. Chem., 1960, 64(382).
20. Chen, N. Y., Maziuk, J., Schwartz, A. B., and Weisz, P. B. Oil and Gas Journal, 1968, 66(47), 147.
21. Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B. Recent advances in the production of fuels and chemicals over zeolite catalysts. Leo Friend Symposium, ACS, August 1977.  
Also: Chem. Tech., 1976, 6, 73.
22. Heinemann, H., Cat. Rev. , 1977, 15(1), 53.
23. Chen, N. Y., Gorring, R. L., Ireland, H. R. and Stein, T. R., Oil Gas Journal, June 6, 1977.

24. Chang, C. D. and Silvestri, A. J. Jour. Catal., 1977, 47(249).
25. Ciapetta, F. G., Dobres, R. M., and Baker, R. W. In P. H. Emmet (Ed.), Catalysis (Vol. 6). Reinhold Publishing, New York, 1958. Pp. 495ff.
26. Mills, G. A., Heineman, H., Milliken, T. H., and Oblad, A. G. Ind. Eng. Chem., 1953, 45(134).
27. Weisz, P. B. and Prater, C. D. Adv. Cat., 1957, 9(575); and Science, 1957, 126(31).
28. Ciapetta, F. G. and Wallace, D. N. Cat. Rev. 1972, 5, 67ff.
29. Klucksdahl, H. E. U.S. Patents, 3, 617, 520; and 3, 558, 477.
30. Sinfelt, H. H. J. Catal., 1973, 29(308).
31. Allison, E. G., and Bond, G. C. Cat. Rev., 1972, 1(233).
32. Flank, W. H. and Beachell, H. C. J. Catal., 1967, 8(316).
33. Thomas, C. L. Catalytic processes and proven catalysts. Academic Press, New York, 1970. Pp. 87ff.
34. Hatch, L. F. Hydrocarbon process 1969, 48(2).
35. EPRI Report AF-190, 1976.
36. Rylander, P. N. Catalytic hydrogenation over platinum metals. New York: Academic Press, 1967.

37. Van Hook, J. P. Cat. Rev., 1980, 20(2).
38. McMahon, J. F. U.S. Patent, 1961, 3, 119, 667.
39. Oblad, A. G., Heinemann, H., Friend, L., and Gamero, A.  
Proceedings of 7th World Petroleum Congress, 1967, 5(197).  
Galliard, Ltd.
40. Moe, J. M. Chem. Eng. Prog., 1962, 58(3), 33.
41. Nielsen, A. Cat. Rev., 1971, 4(1).
42. Royal, M. J., and Nimmo, N. M. Hydrocarbon Process 1969,  
48(3), 147.
43. Kearby, K. K. In P.H. Emmett (Ed.), Catalysis, 1955, 3(453).  
Reinhold Publishing Co., New York.
44. Boundy, R. H., and Boyer, R. F. Styrene. Reinhold Publishing Co.,  
New York, 1952.
45. Lee, E. H. Cat. Rev., 1973, 8(285).
46. Pier, M. Z. Electrochemie, 1949, 53(5), 291.
47. Anderson, R. B. In P.H. Emmett (Ed.), Catalysis, 1956, 4(29).  
Reinhold Publishing, New York.
48. Storch, H. H. Adv. in Cat., 1948, 1(115).
49. Koëlbel, H., Ackermann, and Engelhardt. Proceedings 4th World  
Petroleum Congress, Section 4-C, Paragraph 9, 1959.

50. Koëlbel, H., and Ralek, M. In J. Falke (Ed.), Chemikalische Rohstoffe aus Kohle. Geog. Thieme Verlag, 1977.
51. Office of Coal Research, Department of the Interior, Research and Development Report No. 38, 1968.
52. Mills, G. A. and Steffgen, F. W. Cat. Rev., 1974, 8(159).
53. Miller, S. A. Ethylene and its industrial derivatives. London: Ernst Bern, 1969.
54. Hancock, E. G. Propylene and its industrial derivatives. London: Ernst Bern, 1973.
55. Hearne, G. W. and Adams, M. L. U.S. Patent, 1948, 2, 451, 485.
56. Veatch, F., Callahan, J. L., Idol, J. D., Jr., and Newberger, E. Chem. Eng. Prog., 1960, 56(65).
57. Anonymous. Hydrocarbon Proc., 1967, 46(11), 141.
58. Anonymous. Hydrocarbon Proc., 1967, 46(11), 239.
59. Bedell, K. R., and Rainbird, H. A. Hydrocarbon Proc., November 1971, 141.
60. Spector, M. L., Heinemann, H., and Miller, K. D. I. & E.C. Proc. Res. and Dev., 1967, 6(327).
61. Logan, R. S. and Banks, R. L. Oil Gas Journal, 1968, 66(21), 131.
62. Logan, R. S. and Banks, R. L. Hydrocarbon Proc., 1968, 47(6), 135.

63. Bailey, G. C. Cat. Rev., 1970, 3(37).
64. Parshall, G. W. J. Molecular Catalysis, 1978, 4(243).
65. Wender, I., Sternberg, H. W., Orchin, M. In P. H. Emmet (Ed). Catalysis, 1958, 5(73).
66. Anonymous. Chem. Eng. News, 1961, 39(16), 52.
67. Lowery, R. P. and Aguilo, A. Hydrocarbon Proc., November 1974, 103.
68. Roth, J. F., Craddock, J. H., Hershman, A., and Gulick, F. E. Chem. Tech., 1971, 1, 600.
69. Stobaugh, R. B., Calarco, V. A., Morris, R. A., and Stroud, W.W. Hyd. Proc., 1973, 52, 99.
70. Oblad, A. G. I & EC, 1969, 61, 7, 23.
71. Oblad, A. G., Mills, G. A., and Heinemann, H. In P. M. Emmet (Ed.), Catalysis, 1958, 6, 341.
72. Lenz, R. W. Organic chemistry of synthetic high polymers. Interscience, 1967.
73. Thomas, C. L. Catalytic processes and proven catalysts. New York: Academic Press, 1970. Pp. 72-73.

74. Peters, E. F., Zletz, A., and Evering, B. W. Ind. Eng. Chem., 1957, 49, 1879.
75. Hogan, J. P., and Banks, R. W. U.S. Patent, 1958, 2, 825, 721.
76. Lenz, R. W. Organic Chemistry of Synthetic High Polymers, New York, 1967, Interscience, p. 631.
77. Farkas, A., Mills, G. A., Erner, W. E. and Maerker, J. B., Ind. Eng. Chem., 1959, 51, 1299.
78. Wei, J. Adv. in Cat., 1975, 24, 57.
79. Fickett, A. EPRI Journal, April 1976, 17.